

THE PREPARATION AND DISTRIBUTION OF

ARGONNE PREMIUM COAL SAMPLES*

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ABSTRACT

The eight Argonne Premium Coal Samples were each collected in about 1 1/2 ton quantities, placed in steel drums, purged with argon and taken to ANL for processing. After transfer to a nitrogen filled enclosure, they were crushed, pulverized, mixed and packaged in sealed amber borosilicate ampoules containing 10 grams of -20 mesh or 5 grams of -100 mesh sample. Five gallon carboys hold about 80% of the batch in reserve for filling more ampoules after the original about 5,000 of -20 mesh or 10,000 of -100 mesh samples are depleted. More than 70 laboratories are participating in the analysis. Over 90 shipments have been made to more than 45 different organizations for a range of programs which will be the subject of later papers in the symposium.

INTRODUCTION

The Premium Coal Sample Program is intended to provide the basic coal research community with the best quality samples of a limited number (8) of coals for basic research. The availability of the ampoules is the result of the cooperation of many individuals within a number of organizations whose efforts made the high quality of the samples possible.

The premium coal samples produced from each coal and distributed through this program are chemically and physically as identical as possible, have well characterized chemical and physical properties, and will be stable over long periods of time. Coals have been mined, transported, processed into the desired particle and sample sizes and packaged in humid nitrogen environments as free of oxygen as possible. The need for a Premium Coal Sample Program was expressed on a number of occasions, culminating in the Coal Sample Bank Workshop held March 27 and 28, 1981 in Atlanta, Georgia.

SELECTION OF THE COALS

Support has been provided by the Office of Basic Energy Sciences

to make eight carefully selected coals available. The selection of these coals was based on those parameters which would represent significant differences among the available coals and maximize our understanding of the fundamental properties of coal. A cluster analysis was carried out to establish desirable samples in terms of the significant compositional parameters, C, H, O and S. This was augmented by considerations of maceral content, paleobotanic origins, age and coking properties.

IDENTITY OF SAMPLES AND CHARACTERISTICS

The coals are listed in the order collected. Preliminary data describing the samples are given below. The moisture and ash-free values are given in %, except for sulfur and ash which are in dry %.

#	Seam	State	Rank	C	H	O	S	Ash
1	Upper Freeport	PA	Med. Vol. Bit.	87	5.5	4	2.8	13
2	Wyodak-Anderson	WY	Subbituminous	74	5.1	19	0.5	8
3	Illinois #6	IL	High Vol. Bit.	77	5.7	10	5.4	16
4	Pittsburgh (#8)	PA	High Vol. Bit.	83	5.8	8	1.6	9
5	Pocahontas #3	VA	Low Vol. Bit.	91	4.7	3	0.9	5
6	Blind Canyon	UT	High Vol. Bit.	79	6.0	13	0.5	5
7	Lewiston-Stockton	WV	High Vol. Bit.	81	5.5	11	0.6	20
8	Beulah-Zap	ND	Lignite	73	5.3	21	0.8	6

COLLECTION AND TRANSPORTATION OF SAMPLES

The samples were collected from sites selected in cooperation with the U. S. Geological Survey. The USGS provided technical supervision while a special collection crew from the Pittsburgh Testing Laboratory removed the channel-type sample from each of the underground sites. Usually a fresh block of coal about 18" wide, the thickness of the seam and several feet deep was isolated, removed and placed into stainless steel 55 gallon drums. Surface samples were placed directly into the drums. The drums of coal were placed in a semi-trailer within 1-4 hours from the initiation of the sample collection. The drums were then purged with enough argon gas to reduce the oxygen content to 100 ppm by the same truck driver. The drums were pressurized to 5 psi and taken to Argonne National Laboratory at 42°F, usually within 24 hours.

PREPARATION OF SAMPLES

The drums were unloaded from the truck, weighed and placed into an airlock in a nitrogen-filled processing facility. The oxygen content of the facility was maintained below 100 ppm of oxygen, and typically was about 30 ppm. After the airlock was purged, the drums were opened, and the contents were transferred to a crusher, where the sample was reduced to pieces that would pass between bars with openings 1/2" apart. The crushed coal was

elevated to the pulverizer where it was ground to pass a 20 mesh screen. The entire one-ton batch used for processing was ground and accumulated in a 2000 liter mixer-blender. After thorough mixing the sample was transferred by a tubular conveyor to a second enclosure. About half the batch was transferred to special 5 gallon leverlock pails for transfer back to the initial airlock for later repulverizing to -100 mesh. The balance was mostly placed into 5 gallon borosilicate glass carboys for long-term storage. About 5,000 ampoules containing 10 grams of -20 samples were sealed with a hydrogen-oxygen torch. The flame was kept at the stoichiometric composition with a mass flow controller. The half batch that was transferred to the initial airlock was pulverized to pass a 100 mesh screen and accumulated again in the mixer-blender. After mixing the -100 mesh material was transferred to the second enclosure for placing into 5 gallon borosilicate carboys and into 10,000 ampoules of 5 grams of -100 mesh material. The ANL glassblower sealed the carboys for long term storage. Samples were taken during the processing for homogeneity analyses to establish the uniformity of the samples during the processing and sealing.

One of the samples, the Illinois #6, was taken from the same block of coal which was also collected for the Illinois State Geological Survey. That sample is known as the Illinois Basin Coal Sample Program #5. Larger quantities (1 lb to 50 lbs) of that sample may be obtained from the ISGS.

ANALYSIS OF SAMPLES

The homogeneity samples were irradiated and the induced radioactivity of several isotopes was counted to indicate the content of each species in the samples. A high degree of uniformity was found.

Additional samples have been submitted for a range of analyses including: proximate, ultimate, major and minor elements in the ash, heat content, forms of sulfur, maceral analysis, and reflectance measurements. A large number of laboratories is participating in the analytical studies.

In order to establish the long term stability of the samples, additional analytical work is done including the evaluation of the gas atmosphere inside of the ampoules at two month intervals. For the bituminous samples, Gieseler plasticity measurements are being made to establish the fluidity at various intervals. To date, no indications of oxidation or loss of fluidity have been found.

DISTRIBUTION OF SAMPLES

Samples are distributed as 5 gram ampoules of -100 mesh or 10 gram ampoules of -20 mesh material. Shipments typically involve multiples of 6 or 12 ampoules in special cardboard cartons, with

added foam padding to increase the probability of safe arrival. Orders are sent to the Assistant Controller at ANL, and after processing, are filled and shipped by UPS or international air courier. Order forms may be obtained from the author. A nominal charge of \$8 (US) is made for the 5 gram ampoules and \$16 for the 10 gram ampoules. International shipments involve an additional charge of \$20 for a set of six ampoules.

To date over 89 orders have been filled for more than 3,000 ampoules.

Two types of ampoules have become available during processing. Initially the ampoules were of a standard type with a gradually sloping shoulder to the tip. The "easy-break" ampoules became available later and have been used for the latter coal samples. Instructions for opening the ampoules are included with each shipment. Appropriate care must be exercised in the opening to avoid mixing glass fragments in the coal and to protect the hands of the experimenter.

The importance of mixing must be stressed. All coal samples are subject to segregation on standing. It is necessary to remix the sample before opening the ampoule. The recommended method is to turn the ampoule so that the coal alternately falls into the top and then the body of the ampoule. This should be repeated a number of times (at least 10). Rolling the ampoule on its side is not as effective and should not be relied upon for thorough mixing.

The samples are intended to be used immediately after opening. Any unused portion should be discarded, as the original properties may change on further storage.

RESEARCH BEING DONE WITH THE SAMPLES

The types of research being done with the premium samples includes a cross section of the areas of basic and applied coal research. Some major areas include:

Analytical Studies

A number of analytical studies are being carried out. A direct measurement of organic sulfur by examination of a number of individual coal particles by reflected radiation is being developed. The initial results indicate that the sulfur content of a given maceral may be different than the parent coal but is similar from one maceral particle to another particle of the same maceral. A direct measurement of oxygen is being developed by the use of fast neutron activation, and direct counting of the induced oxygen activity. Corrections are made for oxygen present in the moisture and mineral matter. Several groups are working to establish the relative amounts of the different macerals in

the coal and to separate these macerals. Another group is studying the occurrence of sodium and chloride in the coal to establish the forms in which it may be bound. Still others are using some of the newer instruments, such photoacoustic FTIR to understand the functional groups present in the coal and near the surface. Plasma excitation is being studied to establish the species produced by this technique. Trace element geochemistry is being used to evaluate the relative amounts of the trace elements and to correlate the occurrence of these elements with other factors. One researcher is comparing the carbon found in coal with that found in meteorites.

Physical Properties

The heat capacities of the samples over a range of temperatures are being studied with fresh and aged samples. Interesting differences have been found. The pore characteristics are being studied by a variety of techniques. Solvent swelling studies have also been initiated.

Structure Studies

At least six laboratories are using nuclear magnetic resonance techniques to carry out a variety of structural studies. Several of these will be reported later in the symposium. Chemical techniques are being used by at least three different laboratories. Solvent extraction is being used to evaluate the classes of materials which are present and to determine the effects of aging on the relative amounts of these species. Supercritical extraction is being used at three or more laboratories for similar purposes. The nature and amount of acidic sites is the subject of study at two laboratories. Other workers are using alkylation of sites to establish the effects of altering certain classes of functional groups. Two groups are examining the nature of the water in the coal. Other workers are studying the different forms of sulfur present in the samples to establish the organic and inorganic species which are present. In a number of cases the researchers are using a variety of techniques to probe more deeply into the structural features of the coal material.

Coal Conversion

Pyrolysis is being used at seven or more laboratories to release different species and understand the factors involved in the thermally induced changes. Coal desulfurization by a variety of techniques is another popular area of research. Liquefaction is also being studied at three laboratories with these samples. The catalytic effects on coal conversion is also being evaluated.

The Program Manager is also following the progress of small changes in gas composition of the atmosphere in the ampoules as time passes.

ACKNOWLEDGMENTS

The sponsorship of the U. S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division is gratefully appreciated. The efforts of many who made the program work as effectively as it has must also be mentioned. These include the original planners: Phil Horwitz, John Unik, Randall Winans, Gary Dyrkacz and John Young; the staff of the U. S. Geological Survey who supervised the sample collection: C. Blaine Cecil, Ron Stanton and Peter Warwick; the coal companies who generously made samples available including: Rochester and Pittsburgh Mining Company, Peabody Coal Company, Coteau Properties, Inc.; many involved in the design and construction of the processing facility: Herbert Brown, K. Michael Myles, Gale Teats, Kurt Schultz, Ed Lewandowski, Mike Slawewski, Rich Graczyk, Pat Doolin; the sample collection crew from the Pittsburgh Testing Laboratory: David Allen, Tim Graham, Ron Lowman; the truck driver: Randy Engelhart; those who assisted with the coal processing: Gale Teats, Kurt Schultz, Don Piatak, Wally Czyz, Stuart Janikowski, Freddie Morris, Dmitry Silversteyn, Bart Beals, David Clow, James Krizek, and Mark Kopciewski; the glassblower: Joe Gregar; homogeneity analyses: Bob Heinrich; chemical analyses: Peter Lindahl and Toni Engelkemeir; computer programming by Paul Day and Miriam Bretscher; purchasing by Joe Forzley and Ronette Stachelski.

SMALL ANGLE NEUTRON SCATTERING STUDIES OF SWELLED COAL

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INTRODUCTION

The objective of this study is to determine changes that occur in the physical structure of coals upon swelling in an organic solvent. It is known that bituminous coals will swell in solvents such as pyridine (1). The phenomenon of coal solvent swelling is being used to characterize coal structure especially in the determination of molecular sizes between cross-links. Swelling can affect coal reactivity in thermolysis reactions. Also, it is important to note that swelling increases reagent accessibility in chemical modification of coals (2). Small angle neutron scattering (SANS) is the approach used in this study to examine the changes in pore structure in a Pittsburgh #8 seam hvA bituminous coal, Argonne Premium Coal Sample #4 (3). Two perdeuterated solvents are used, benzene for non-swollen and pyridine for swelling conditions. The deuterated solvent provides a large contrast between the solvent and the solid coal for neutron scattering.

Coal porosity has been studied by SANS in the dry state (4,5,6) and in non-swelling deuterated solvents (4,6). These studies suggested that this technique can be useful for examining pore structure. Our current results show that the pore structure of a coal swollen in pyridine is dramatically altered from its original state.

EXPERIMENTAL

The SANS measurements were made at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS) using the Small Angle Diffractometer (SAD). Neutrons were produced in pulses by spallation from 450 MeV protons followed by moderation by solid methane (18°K) to produce wavelengths of 0.5 to 14 Å. The sample saw a 0.9 cm diameter beam. A 64x64 array position sensitive multidetector was used to detect neutrons scattered by the sample while the wavelength of the neutrons (λ) was determined by time-of-flight. The data were corrected for scattering from the cell and incoherent scattering. Finally, the intensity (I) was expressed as a function of the scattering vector, Q:

$$Q = (4\pi/\lambda) \sin \theta \quad (1)$$

where θ was half the scattering angle and:

$$I(Q) = K \int_V (\rho_s - \rho_m) \exp(iQr) d^3r \quad (2)$$

where K included all the experimental constants and ρ_s and ρ_m were the scattering length densities of the solvent and the matrix. A Q range of 0.005 to 0.35 Å⁻¹ was accessible on the SAD instrument at IPNS.

The preparation of the Argonne Premium Coal Sample has been described (3). A -100 mesh APCS #4 sample was used. (Preliminary analytical data, on a maf basis: C 83%, H 5.8%, N 1.6%, O 8% S(dry) 1.6% and ash(dry) 9%.) A sealed glass ampoule containing the coal was broken open in a nitrogen atmosphere glove box. The coal was well mixed and a portion transferred to a 2 cm diameter x 1.85 mm thick quartz cell leaving enough room for swelling. Perdeuteriosolvent was added to the coal and then the cell was sealed. The sample was allowed to sit for several days before doing the SANS experiment to insure complete swelling in the case of d_5 -pyridine.

RESULTS AND DISCUSSION

A Guinier plot (7), based on the relationship shown in Equation 2, for both solvents is shown in Figure 1. Even though d_6 -benzene and d_5 -pyridine have similar scattering length densities, 5.35 and $5.69 \times 10^{10}/\text{cm}^2$ respectively, there is a striking difference between the scattering data from the two solvents. The scattering data for both solvents exhibit a steep slope at low Q . These results are indicative of large pores with sizes up to 1000 \AA . The largest pores that have been reported previously had a 500 \AA limit which was constrained by the instrumentation (1). Further analysis of the d_6 -benzene data shows a distribution of pore sizes from 12 \AA up to the 1000 \AA limit. The difference of the porosity between the coal and swollen coal may be in the shape of the pores.

In low angle scattering it is possible to determine the shape of the pore or particle using a modified Guinier analysis (7). There are three types of pore shapes: spherical, elongated (tubular) and lamellar. From the Guinier analysis one can determine the radius for spherical, cross sectional radius and length ($1/Q$) for elongated, and thickness and area ($1/Q^2$) for the lamellar shapes due to the following scattering laws:

$$\text{Elongated: } I = I_c \cdot 1/Q$$

$$\text{Lamellar: } I = I_c \cdot 1/Q^2$$

To investigate the possibility of elongated pores $\ln(I \cdot Q)$ is plotted versus Q^2 in Figure 2. For d_6 -benzene there is no correlation, but for the d_5 -pyridine a negative slope is found. At low Q tubular pores with a radius of $9\text{--}11 \text{ \AA}$ are found. Figure 3 shows that lamellar pores are not seen in either sample since positive slopes are observed for both samples.

From these preliminary results we conclude that in a good swelling solvent the tertiary structure of this bituminous coal undergoes major rearrangement. Whereas the original coal contains a broad size range of roughly spherical pores, the swollen coal contains elongated pores with several distinct sizes. The pyridine appears to be determining the new pore dimension. Exactly five pyridines can be fitted into a 9 \AA radius circle as shown in Figure 4. Table 1 lists the dependence of pore radius on the number of pyridines packed into a cross-section of the elongated pore. The size of the pyridine molecule has been estimated from space-filling computer models based on the van der Waals radii of the individual atoms. Even at high Q , up to the instrument limit, a negative slope for the modified Guinier analysis is

TABLE 1. Possible Packing Arrangements of Pyridine Molecules in Tubular Pores

Number of Pyridines	Radius of Pore (Å)
1	3.37
2	6.74
3	7.26
4	8.14
5	9.10
6	10.11
7	11.14

observed giving a radius of approximately 6 Å. This size of tubular pore could accommodate stacks of two or three pyridine rings. It is important to note that we are observing relative narrow elongated pores. These results could be explained by invoking hydrogen bonding between the pyridines and the phenols or other acidic hydroxyls on the surface of the tubular pores. In addition, it is thought from the NMR and ESR experiments that the motion of pyridine in a coal is restricted (8). Our SANS data argues against a layered, polycyclic aromatic structure for this coal. Possibly hydrogen bonding is more important in determining the tertiary structure.

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Figure 1. Guinier plot for SANS of the Pittsburgh #8 Bituminous coal, APCS #4

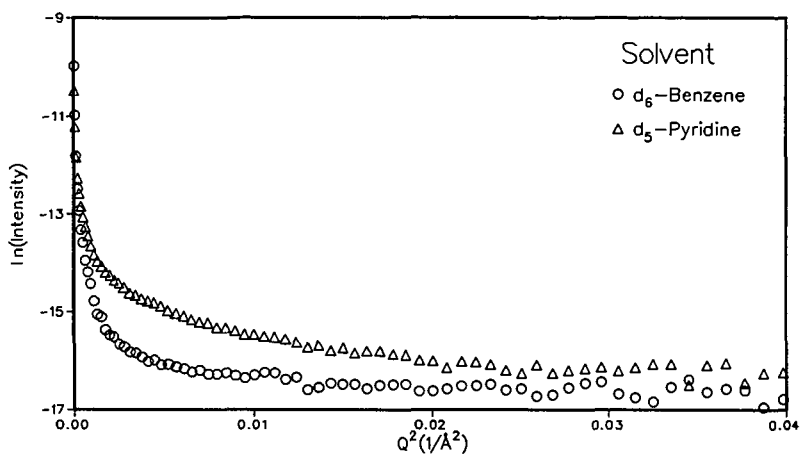


Figure 2. A modified Guinier plot of SANS data for APCS #4 to evaluate the possibility of tubular pores

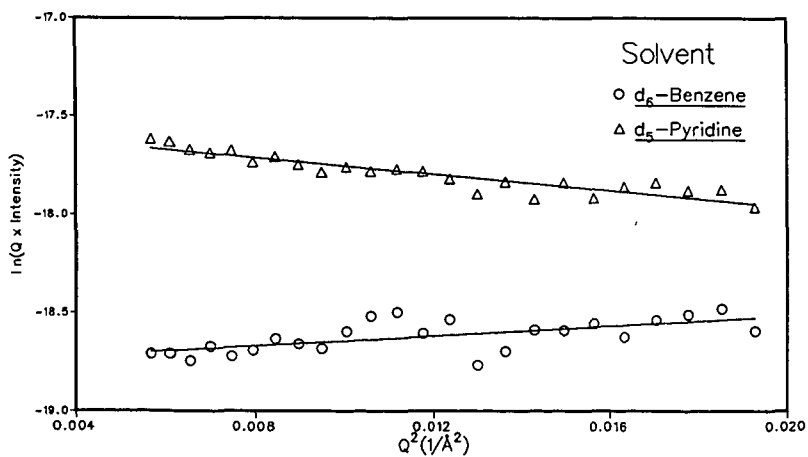


Figure 3. A modified Guinier plot of SANS data for APCS #4 to evaluate the possibility of sheet-shaped pores

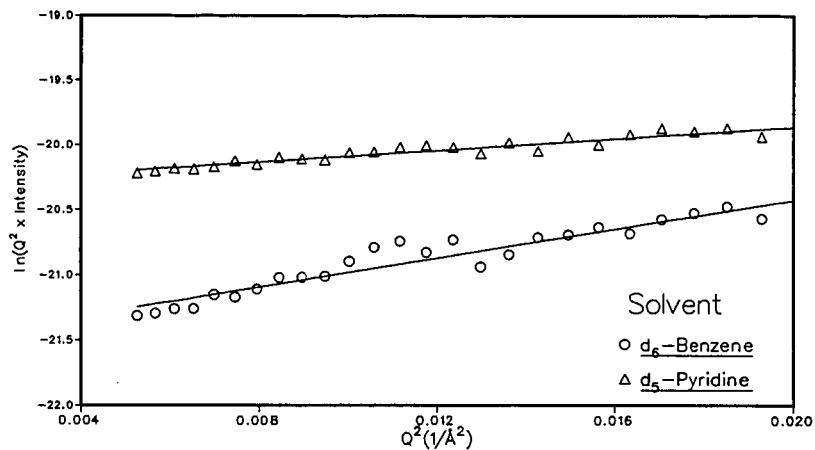
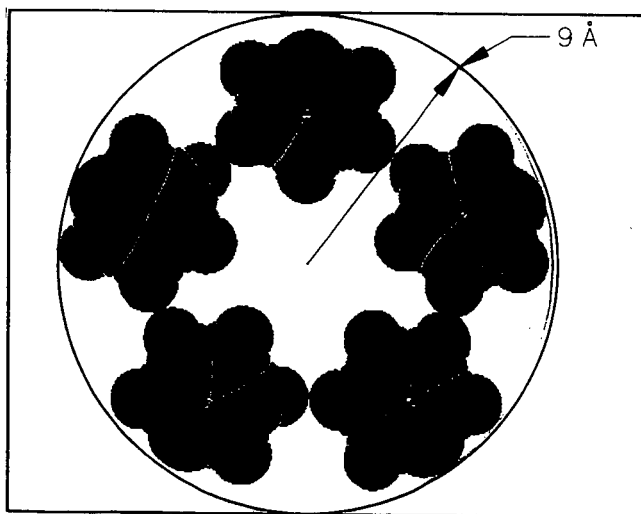


Figure 4. Possible arrangement of five pyridine molecules in a 9 Å radius elongated pore.



A Possible Connection Between Gas Solubility in Coals and BET Surface Areas

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INTRODUCTION

Gas adsorption techniques have been widely used in determining surface areas of porous and nonporous solids. The surface areas of coals, calculated from nitrogen isotherms at 77.8°K, are considerably less than those obtained using CO₂ at 195°K.^{1,4} It is generally believed that N₂ yields low surface areas because the micropores in the coals are not completely accessible to N₂ at 77.8°K. Limitations are imposed by an activated diffusion process for N₂ and/or shrinkage of the coal pores at 77.8°K.^{1,4} Carbon dioxide has a lower activation energy for adsorption than N₂.^{1,5,6} It has been suggested that CO₂ interacts with oxygen functionalities in coals resulting in swelling which may contribute to the large surface areas for coals.

As part of another investigation, we have measured BET surface areas of a high volatile bituminous coal with small hydrocarbon gases expected to be insoluble in the coal. We report here a comparison of these surface areas with those obtained using CO₂ and Ar. We tentatively conclude that the solubility of CO₂ in coals is important in that it gives CO₂ access to closed pores which are otherwise ignored in surface area measurements by gas adsorption. It may be that the majority of the coal surface area lies in closed pores.

EXPERIMENTAL

A high volatile Ill. No. 6 coal sample (100 mesh, 75.2% C, 4.5% H, 1.4% N, 3.3% O, 2.4% S all dmmf) was obtained from the Premium Coal Sample Bank at Argonne National Laboratory. 100 mg samples of this coal were transferred into a preweighed sample container in a nitrogen filled glovebox for each experiment. The samples were outgassed on a glass BET isothermal apparatus under a vacuum of approximately 10⁻³ torr for no less than 8 hrs. A Datametrics Barocel pressure sensor was used to measure the pressure drop from a known volume to the sample container. The dead volume of the sample container was determined by the pressure difference of He from the known volume to the sample container at 77.8°K. This instrument has given correct surface areas for standard materials.

RESULTS AND DISCUSSION

The surface areas we obtained using Ar and CO₂ (Table I) are consistent with those reported for Ill. No. 6 coal by others.^{2,4} The astounding feature of the data in Table I is the very low surface area obtained with cyclopropane. It is considerably less than the surface area given by CO₂. Cyclopropane and CO₂ have the same cross-sectional area when they are determined by the method of Emmett and Brunauer. The cross-sectional area of cyclopropane₂ calculated from its structure and standard bond lengths is 23.2 Å² if it lies flat and 20.3 Å² if it lies on a side. These are close enough to the calculated value and to each other to have no effect on our conclusions. Since the molecules are of similar size, it is difficult to rationalize the very large surface area differences using arguments based on molecular sieving by the pore system. When an adsorbate molecule is soluble in the coal, the surface area increases with solubility (Fig. I, work by Reucroft and Patel, ref. 2). On this basis, it is possible that the low surface areas observed with nitrogen (Table II), CCl₄, and n-hexane (Fig. I) are all correct and the surface area obtained from CO₂ is in error due to its solubility in the coal. We disagree with this. The solubility of CO₂ in coals is not great enough to explain the large surface areas observed and CO₂ surface areas agree well with those obtained using X-ray scattering.¹¹ It seems likely that the CO₂ surface areas are approximately correct for coals and we must seek an explanation for the anomalously low surface area obtained with cyclopropane.

If the CO₂ surface areas are approximately correct, then CO₂ must be able to reach coal surface which is inaccessible to cyclopropane. This brings us to consider the solubility of the two gases in coals. The solubility of CO₂ in coals has been experimentally demonstrated (see however ref. 10). Cyclopropane is probably insoluble in the coal. It has been established that alkanes do not swell coals to any appreciable extent and the heats of wetting of coals by alkanes is zero.^{11,12} We conclude that cyclopropane is probably insoluble in the coal.

This solubility difference is the basis of an explanation of the different surface areas obtained with these two gases. If a large portion of the pores in coals are closed, they will remain inaccessible to molecules unable to dissolve in coals. The pores are not directly connected to the external surface so a molecule must dissolve in and diffuse through solid coal to reach the closed pores. Adsorbate gases capable of dissolving the coal have accessibility to pores that are closed to insoluble molecules. Thus, soluble CO₂ gains access to all of the pores in this coal while insoluble cyclopropane can only reach those connected to the exterior by the pore network. If this is correct, most of the coal pore system is closed.

It can be argued that the coal is shape selective and that the rod-like CO₂ molecule can penetrate the pores while the flat

cyclopropane cannot. Work with amines has shown that planar molecules easily penetrate coals while branched molecules do not.¹³ It has been shown that both n-butane and CF_2Cl_2 also give low coal surface areas.^{14,15} If coals are shape selective, they are extraordinarily discriminating. Molecules such as methanol which interact specifically with coals and dissolve in them report very large surface areas which are incorrect.¹⁵ What is being measured is solubility in the coal, not surface area. It seems to us most reasonable to conclude that coal pores are mostly closed and inaccessible to molecules not soluble in the coal.

With this model there are three classes of sorbed molecules. Molecules which interact specifically and strongly with coals or which are soluble in coals report very large and meaningless surface areas. The experiment measures their solubility in the coal. Molecules which are insoluble in coals can be used to measure that part of the surface area which is open to the surface and accessible to the probe molecule. This accessibility is governed by the pore size, the molecule size, and the temperature since diffusion may be activated. Finally, there are those molecules whose solubility in coal is low, but which can penetrate all of coal by virtue of that solubility. These molecules will have access to all of the pores, even those not connected directly to the surface, and can be used to determine an approximately correct total surface areas.

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Table I. Surface Areas of Ill. #6 Coal

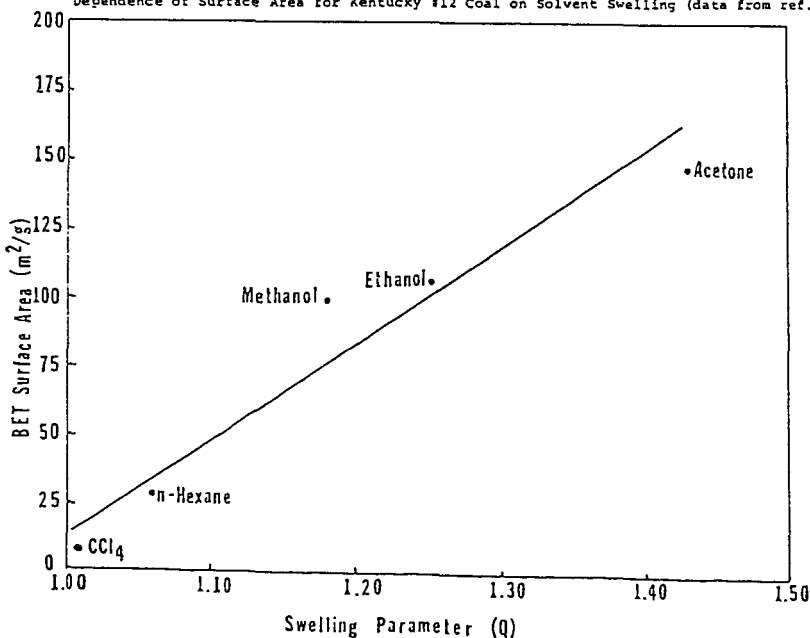
Adsorbate	Adsorption Temperature (°K)	Cross-Sectional Area (Å ²)	BET Surface Area (m ² /g)
Argon	77	16.2	14
			15
Carbon Dioxide	178	25.3	132
			132
Cyclopropane	203	25.2	36
			31

Table II. Surface Areas of Kentucky #12 (from ref.2)

Adsorbate	Cross-Sectional Area (Å ²)	BET Surface Area (m ² /g)
Nitrogen (77.8°K)	16.27	4
Carbon Dioxide	25.30	101

FIGURE I.

Dependence of Surface Area for Kentucky #12 Coal on Solvent Swelling (data from ref.2)



SPECIFIC HEAT MEASUREMENTS OF TWO PREMIUM COALS

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Introduction

Our purpose in initiating the study of the premium coal was threefold. Our first aim was to observe the behavior of the premium coal. Second, we wished to obtain reliable heat capacity data to add to the pool of available information on the premium coals and thus extend the data base available for the development of useful correlations. Third, we wished to compare the results obtained for premium coals with those obtained on a nonpremium coal during our development of transferable measurement techniques. The heat capacity measurements made on the nonpremium coals had shown the development of a deep exotherm on initial heating as the coal became more oxidized. We surmised that the difference between the initial and repeat measurements on the oxidized coal could be ascribed in some way to the increased oxidation level of the nonpremium coal. However, the contributions to that effect were not clear.

The heat capacity measurements have been made in sealed cells with no significant mass loss. Water has been shown to be released from the coal as it is heated above the temperature at which it was dried in the course of specimen preparation.(1,2) Three possible sources of this water have been identified. First, it may be water physically trapped in the coal structure that is released as the coal is heated above its drying temperature. Second, the water could be produced by mineral reactions that occur as the coal is heated. Carling has applied a thermodynamic predictive program, which identifies the most likely mineral reactions at various temperatures, to the nonpremium coal used in our studies.(3) Reactions that produce significant amounts of water are predicted to occur between 400 and 450 K, which is within the range of our measurements. Third, the water may be generated by condensation reactions occurring within the organic component of the coal. These would increase as the coal becomes more oxidized.(4)

One possible contribution to the deepening of the exotherm with increased oxidation was the increased exothermicity expected on readorption of water on a more oxidized surface. Barton has evaluated the effects of increased oxidation on the enthalpy of adsorption of water on coal surfaces.(5)

Two investigations in our laboratory have shed light on the causes of the observed exotherm: The heat capacity of both premium coals and

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macerals have been measured. Measurements on the macerals will allow separation of the mineral contributions from those of the organic moieties of coal. The studies on the premium coal aid in the evaluation of the effects of oxidation. It is the studies of the premium coals which are discussed in this contribution.

Experimental

(i) Materials

The premium coals used in this study were the medium volatile bituminous coal from the Upper Freeport Seam and the high volatile bituminous coal from the Pittsburgh #8 Seam.(6) The Upper Freeport Seam coal was the first of the premium coals available and was obtained at the very beginning of this study. During the analysis of the results of these measurements it became evident that measurements on a high volatile premium coal would be most helpful and the Pittsburgh Seam coal was obtained. Comparisons are made with measurements on a high volatile Colorado coal, PSOC-854, that was obtained from the Coal Sample Bank at Pennsylvania State University. The as-received oxygen content of the premium coal was less than two percent; for the nonpremium coal, it was 11 percent.

(ii) Sample preparation

The premium coals were opened in a controlled-atmosphere chamber with low oxygen and moisture levels.(7) They were dried to constant weight at 383 K in a stream of dry nitrogen; the premium coals reach constant weight within 24 hours. The sample is then riffled to ensure representative sampling. The coal is pelletized and sealed in an inert atmosphere within the controlled-atmosphere chamber. Specimen masses ranged from 11-25 mg. Forty specimens of each coal were prepared. Some were used in the initial studies reported here; other, sealed at the same time under the same conditions, are available for further work.

(iii) Measurements

Heat capacity measurements were made in sealed cells with a power-compensated differential scanning calorimeter (DSC) over the temperature range 300-520 K at a heating rate of 5 K/min. Calorimetry Conference sapphire was used as a standard.(8) The heat capacity of the sapphire standard, determined before beginning the measurements reported here with the instrument settings to be used, was accurate to ± 1.5 percent. Heat capacity measurements were made on 20 specimens of the Upper Freeport Seam coal; 10 specimens of the Pittsburgh Seam coal were used.

The standard operating procedures and data acquisition and reduction methods used for heat capacity measurements in our laboratory have been described.(9) Modifications have been made to these procedures for a material that undergoes an irreversible reaction on the first heating.(10)

The moisture content of the specimens as used was determined by means of a thermogravimetric balance (TGA).

Results and Discussion

In Figure 1 the heat capacities of the Upper Freeport Seam coal, for both initial and repeat runs, are shown. For purposes of comparison, similar measurements on an oxidized coal, PSOC-854, are shown in Figures 2 and 3. Though this coal, not a premium coal, had an as-received oxygen content of 11 percent, it was ground to -100 mesh in our laboratory before we had the capability of protecting it from the atmosphere. Because it was already well-oxidized when our protective facility was ready, no attempts were made to prevent further oxidation. The moisture content of the specimens actually measured, as determined by TGA, was less than 0.3 percent.

A significant difference between the premium and the nonpremium coals is evident on comparison of Figures 1, 2 and 3. The premium coal does not exhibit the deep exotherm on initial heating that is observed for the nonpremium coal. Both coals manifest expected, or normal, heat capacity behavior on the repeat runs. Differences between initial and repeat runs similar to those for the oxidized coal have also been reported by Singer and Tye(11) and by Richardson.(12) The differences noted strengthen our supposition that the exotherm is associated with the increased oxidation level of the coal.

The exotherm is now believed to result from exothermic condensation reactions which occur on the oxidized coal surface.(4) In the course of development of measuring techniques which will give valid results universally (transferable measuring techniques) we have made heat capacity measurements during several years on the PSOC-854 coal. As the coal has become more severely oxidized, the exotherm has deepened. A quantitative evaluation of the exotherm for coal specimens sealed in an inert atmosphere shows an increase from 6 J/g for a coal containing minimal amounts of oxygen to 38 J/g for a severely oxidized coal. For coals sealed in air, the enthalpy difference between initial and repeat runs is 60 J/g. The small energies stated here, when translated to tons, of coal are on the order of 5-34 MJ.

As our measurements were made in sealed specimen cells, the possibility of a contribution from readsorption of water exists. The water that was released during the heating of the coal to a temperature above that at which it was dried has the potential to react with the altered coal surface. Barton has shown that the exothermicity of the enthalpy of adsorption of water on a coal surface increases significantly as the coal becomes more oxidized.(5)

Another contribution to the differences observed between initial and repeat runs on premium and nonpremium coals arises from the difference in the volatile matter content of the two coals studied. Proximate analysis of the medium volatile premium coal gives a volatile matter content of 32 percent; for the high volatile coal, it gives 43 percent. In analyzing the results of measurements on the Upper Freeport seam (a

medium volatile coal) and comparison with the PSOC-854 coal (a high volatile coal) the effects of the difference in volatile matter content of the two coals were of concern.(4) These effects, however, could not be evaluated until measurements on a premium high volatile coal were completed. The Upper Freeport Seam coal was the first of the premium coals to be distributed and was the only one available at the time this study was initiated. A sample of a high volatile premium coal (Pittsburgh #8 Seam) has since been obtained; measurements in progress on this coal will permit the effects of volatile matter content to be assessed.

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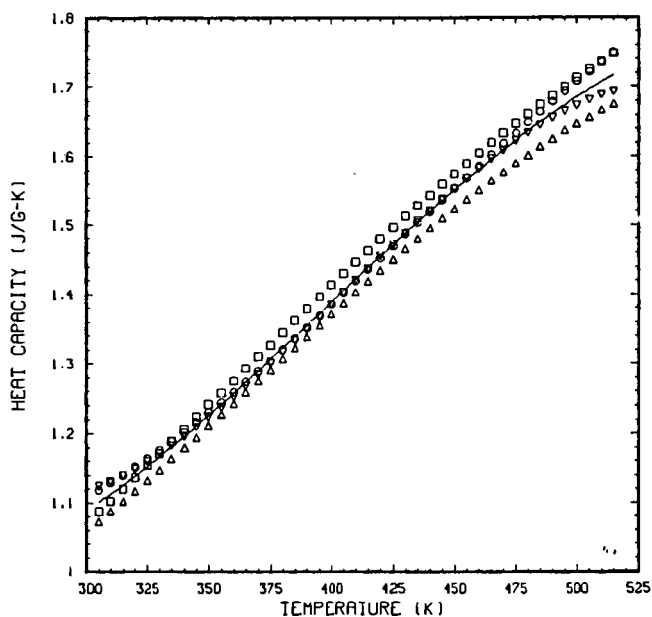


Figure 1. Initial and repeat measurements of premium coal. Fitted value for all measurements, —; fitted values for sets of five replicates, symbols; repeat measurements, Δ ; initial measurements, other symbols.

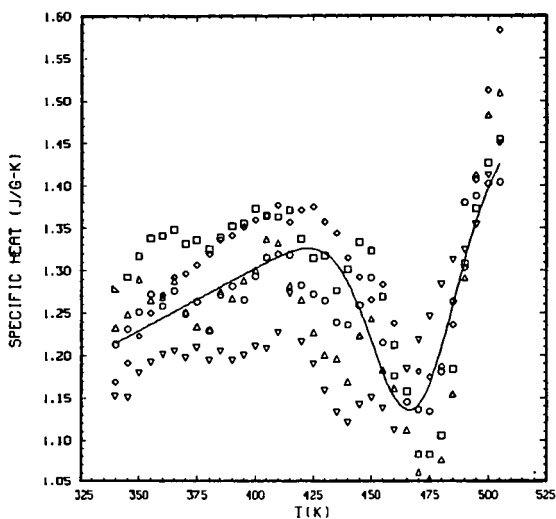


Figure 2. Initial measurements on nonpremium coal. Fitted value for five replicates, \square ; individual measurements, symbols.

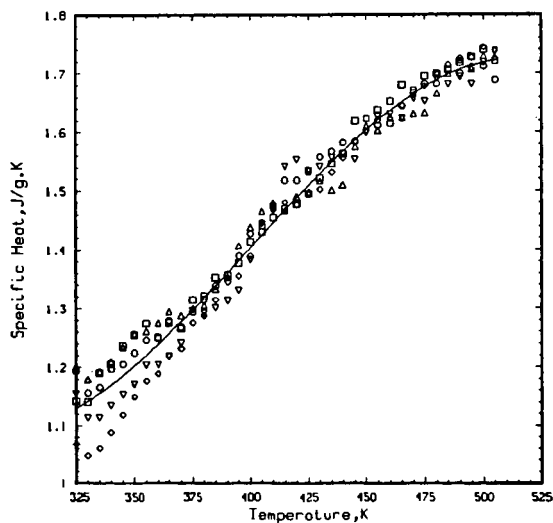


Figure 3. Repeat measurements on nonpremium coal. Fitted value for five replicates, \square ; individual measurements, symbols.

HEAT CAPACITIES OF ARGONNE PREMIUM COAL SAMPLES

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INTRODUCTION

The thermal effects on coal have been the subject of numerous investigations dating back to the 1890's. (1) Many techniques have been used to study thermal effects, including differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetric analysis. DTA and DSC studies of coals by different researchers yield conflicting information (2-5). Numerous heat capacity determination (6-11) have been done on coals over the years. However in these investigations no particular care was taken to check the effects of "weathering" on the measured parameters. A number of the coals investigated were the same as those which are part of the Argonne Premium Coal sample series.

In this communication we report the results of recent DSC investigations on the Argonne Premium Coal Sample series. In these experiments care was taken to correlate the heat capacity with the thermal history of the specimens.

EXPERIMENTAL PROCEDURE

Differential scanning calorimetry was used to determine the response of coal samples to heating. Heating rates of 10K/min. were used. Sample sizes were of the order of 10 to 15 milligrams. Temperatures for the measurements ranged from 100K to 700K. All experiments were done under flowing nitrogen (1 stp l/min.), and the exposure of the samples to the ambient environment was limited to less than two minutes. The heat flow curves were obtained while maintaining constant experimental conditions. The uncertainty in the reproducibility of the data is estimated at one percent. Heat capacities were calculated from the heat flow curves, using sapphire as a standard for comparison. The error in the derived heat capacities is estimated at two percent.

RESULTS AND DISCUSSION

Coal is a complex mixture of organic matter, inorganic matter and water. The usual way of correlating the coal heat capacity data as a function of temperature is to follow Kirov's (6) procedure of expressing the total heat capacity as a weighted sum of the heat capacities of fixed carbon, volatile organic matter, ash and water. Implicit in Kirov's method are the assumptions that these components do not interact, and up to the pyrolysis temperature, the coal does not undergo either a chemical reaction or a structural rearrangement. However, there are a number of experimental findings which bring these assumptions into question.

Mraw (12) has measured the heat capacities of coals as a function of water content and found that one must consider the water associated with a

coal to be composed of two types: freezable water, which forms a liquid layer adsorbed on the coal and nonfreezable water which resides in the form of molecular clusters in the pore structure of the coal. The nonfreezable water contributes an excess low temperature heat capacity to the coal due to the onset of rotational and vibrational motions of the clusters inside the pores.

Measurement of coal char heat capacities (13) and of coal ashes (14) indicate that the heat capacity of the char is not a weight-average sum of the ash free char heat capacity and of the ash heat capacity. Thus, there is additional evidence that Kirov's correlation method must be reconsidered. Furthermore, as noted in the introduction, many coals undergo both endothermic and exothermic reactions at temperatures prior to the onset of pyrolysis breakdown. Therefore, it is even questionable that a meaningful heat capacity can be assigned to a coal at temperatures past the onset of reactions accompanied by thermal effects.

In Figure 1, the heat absorption rate ($\text{kJ kg}^{-1} \text{sec}^{-1}$), \dot{Q} , for the Wyoming Sub-bituminous coal is shown as a function of temperature. These data are derived from the heat flow curves for a given sample by dividing the heat flow (milliwatts) versus temperature curves by the weight of the residual sample at the maximum temperature of a given run. The particular features of the figure to be noted are:

- * An endothermic peak at low temperatures due to the "pore" water present;
- * Melting and evaporation of the "freezable" water extending over a wide temperature range. This endotherm would mask any other endotherm occurring in the same temperature range;
- * Start of an exotherm around 400K;
- * An endothermic reaction between 575K and 675K.

In the above context endothermic and exothermic are defined as heat absorption relative to that which would be calculated from the heat capacity versus temperature curve for a non-reactive sample. Such an absorption curve is indicated on the figure.

By repeating the heating curve for the same sample we note the disappearance of the endothermic peaks associated with water desorption and the reduction and eventual disappearance of the high temperature endotherm. The exotherm also decreases in magnitude, at a given temperature with recycling. The sample loses weight on heating. The total weight loss is 55% of the starting weight. The major portion (40-48% of starting weight) of the weight loss is due to the removal of water.

In Figure 2 we show the heat absorption rate versus temperature data for a sample of the Pittsburgh #8 High Volatile-bituminous coal. This coal has much less water. The total weight loss of 3% is almost totally due to water loss. Inspection of Figure 2 shows the existence of a low temperature endotherm starting at 300K. This endotherm persists after the removal of the water and blends smoothly into the exotherm starting about 400K.

Even stronger evidence for the existence of a low temperature, nonwater-related endotherm preceding the exotherm is seen in Figure 3 for the Pocahontas #3 Low Volatile-bituminous coal. For this coal there is no weight loss observed, but a well defined endotherm is seen starting at 300K.

It is our belief that the low-temperature endotherm followed by exothermic behavior is associated with a free-radical polymerization reaction in the coal. Petrakis and Grandy (15) have reported that a substantial number of free radicals are present in coal heated between 375 and 700K. We feel that the 300K to 400K endotherm is associated with free-radical formation. The recombination of the free radicals is sufficiently exothermic that the overall behavior is exothermic above 400K. The overall reaction is rather slow and does not approach completion in the time span of the experiment.

The high temperature endotherm could be due to either the softening of the partially reacted coal and/or to bond-breaking reactions in the unreacted coal. Previous studies (16) have shown that the reaction is reversible as long as the material is kept below 630K. Hydrogen bond-breakage has been postulated (4) as a source of this endotherm. However, additional free-radical formation can not be ruled out. If the coal is pretreated in flowing steam at around 610K it yields more volatile products during steam pyrolysis at high temperatures (17). But if the pretreated coal is exposed to air (O_2) even for a few minutes the steam pyrolysis yield of the coal reduces to levels below that of untreated coal.

The heat absorption curves of the other coals are qualitatively similar to those shown. The major differences between the coals, are due to the difference in water content, the progressive reduction in the magnitude of the exotherm at a given temperature as the rank (carbon content) of the coal increases.

Heat capacity data can be extracted from the heat absorption rate curves using the relation:

$$C_p(T) = \dot{Q}(T)/\dot{T}(T) \quad 1)$$

where $C_p(T)$ is the heat capacity in $\text{kJkg}^{-1}\text{K}^{-1}$ at a given temperature and $\dot{T}(T)$ is the actual (determined) heating rate at the same temperature.

In our experiments $\dot{T}(T)$ is nominally 0.1667 K/sec. However, for each experiment the actual heating rate was determined by running the heat absorption rate curve for a sapphire standard under the same exact experimental conditions as those for the sample runs.

The heat capacities were calculated based on the assumption that up to 270K there is no weight loss on heating. The heat capacities above 300K were calculated by extrapolating the heat absorption rate curves which would have been obtained in the absence of heat absorbing or heat releasing reactions. The calculated heat capacities are shown in Figure 4 and are also tabulated in Table 1.

There was no general trend with coal rank observable in the heat capacities. This was not, surprising since the heat capacity was not

separated into contributions due to the organic, inorganic and water components.

At the present time (May 1987) work is still in progress to complete the data for the rest of the Argonne Premium Coal Sample series, to prepare and measure ash heat capacities, and to investigate the effect of accelerated weathering on the heat absorption rates and on the heat capacities.

Table 1. Heat Capacity ($\text{kJkg}^{-1}\text{K}^{-1}$) of Argonne Premium Coals

Temp (K)	Wyoming	Illinois #6	Blind Canyon	Pittsburgh #8	PA-Up. Freeport	Pocah. #3
	Sub-bit	HV-bit	HV-bit	HV-bit	MV-bit	LV-bit
100	0.179	0.325	0.485	0.410	0.396	0.256
125	0.307	0.466	0.660	0.574	0.605	0.762
150	0.503	0.584	.815	0.683	0.667	0.969
175	0.727	0.760	0.902	0.800	0.698	1.137
200	0.973	0.958	1.001	0.956	0.799	1.241
225	1.312	1.251	1.121	1.103	0.882	1.270
250	1.841	1.515	1.159	1.169	0.970	1.333
275	1.771	1.481	1.206	1.228	1.075	1.348
300	1.415	1.277	1.252	1.281	1.156	1.355
325	1.244	1.167	1.219	1.364	1.070	1.390
350	1.307	1.237	1.267	1.409	1.205	1.411
375	1.355	1.270	1.332	1.459	1.265	1.432
400	1.389	1.317	1.351	1.500	1.315	1.453
450	1.463	1.363	1.423	1.573	1.385	1.480
500	1.507	1.422	1.494	1.646	1.450	1.508
550	1.559	1.443	1.538	1.701	1.486	1.522
600	1.576	1.467	1.577	1.756	1.534	1.536
650	1.608	1.511	1.618	1.792	1.548	1.543
700	1.609	1.514	1.650	1.828	1.586	1.550

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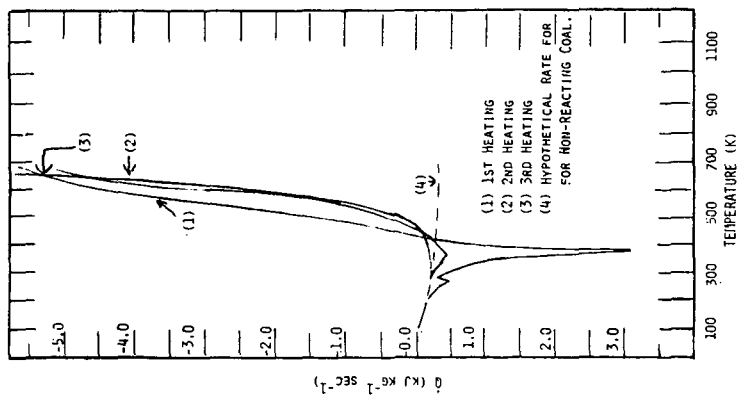


FIGURE 1. WYOMING SUB-BITUMINOUS COAL; HEAT ABSORPTION RATE.

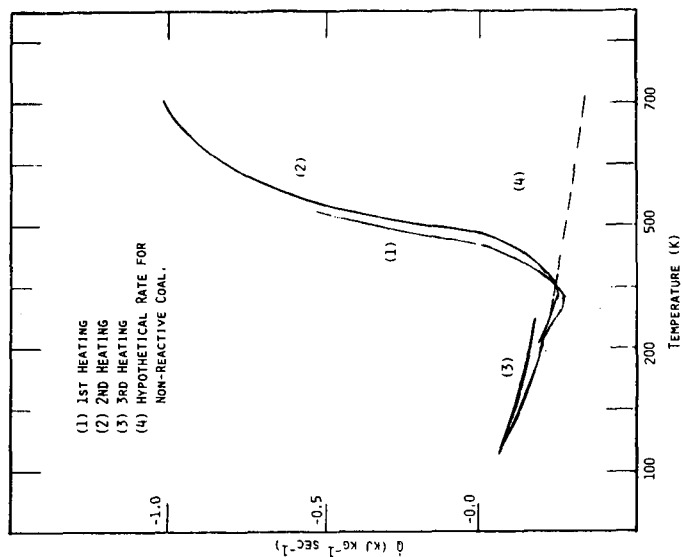


FIGURE 2. PITTSBURGH #8 COAL; HEAT ABSORPTION RATE.

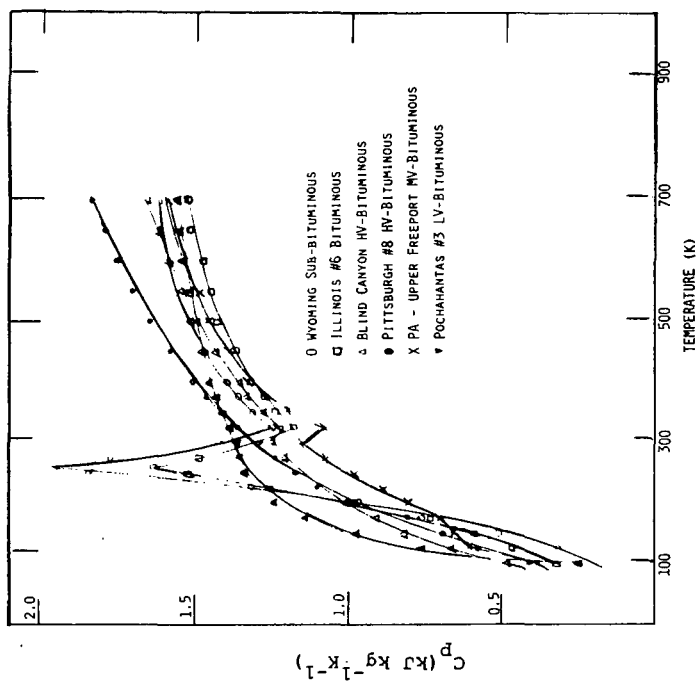


FIGURE 4. HEAT CAPACITY OF ARGONNE PREMIUM COALS.

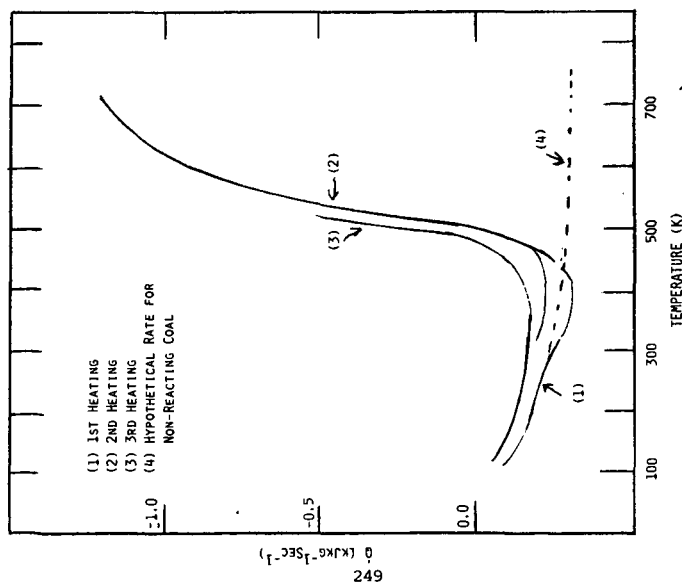


FIGURE 3. POCAHONTAS #3 COAL; HEAT ABSORPTION RATE.

Spatial Variation of Organic Sulfur in Coal

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INTRODUCTION

Spatial variation of organic sulfur concentration in coals has been generally known for years. The high resolution of the transmission electron microscope permits that variation to be measured more precisely than is possible by bulk techniques; variations may be measured over distances less than 1 μm .

Measurement of organic sulfur content using the transmission electron microscope requires use of ultra thin films or very fine powders. We typically use foils less than 1 μm thickness or powders ground to a few μm . The organic sulfur content is proportional to the ratio of the count rate for the sulfur K α line to the count rate for the background radiation measured over some convenient energy interval. The proportionality constant is determined using sulfur standards. The technique is highly reliable for sulfur, as is shown in earlier publications (1-3). The PIXE method for heavier elements also utilizes the background radiation to permit absolute numerical concentrations to be derived.

This paper reports a particular application of the TEM method to determination of the spatial variation of organic sulfur, both within a given maceral and among maceral types. Some of the observations report measurements on powdered specimens, others on foil specimens prepared from bulk coal.

SPATIAL VARIATION

We have reported several measurements of the spatial variation of organic sulfur in coal. We cite two new measurements here. The variation in organic sulfur content of a sporinite maceral embedded in a larger vitrinite maceral in an Illinois #5 coal is shown in Fig. 1. Several features are evident. A considerable variation exists across a maceral, but an even larger variation exists between the two macerals. The sporinite maceral has a much higher concentration of organic sulfur than of the vitrinite. In contrast, resinite commonly has a lower organic sulfur content than vitrinite in a particular coal. This is evident from the data in Fig. 2 for a resinite maceral embedded in vitrinite in a block of Illinois #6.

MEASUREMENTS ON WHOLE COALS

Many measurements have been made of the organic sulfur content of whole coals, both to find the spread in sulfur content and to determine the average organic sulfur content. A number of these coals have been from the Argonne Premium Coal Bank. We show in Fig. 3 the sulfur distribution obtained for seven of these coals. The concentration varies widely for each of the coals. We have not separated these coal into maceral types, so we do not know

the variation by maceral type. We have reported measurements on other bituminous coals separated into maceral fractions, though, and report such an observation in the next section.

Measurements on individual particles of a coal have considerable variation as the data of Fig. 3 show, but the average over a number of independent measurements has been found to be very close to the average organic sulfur content of that coal determined by bulk methods. A comparison made between eight coals measured in the TEM and the reported organic sulfur content measured by ASTM methods independently shows good agreement, Fig. 4.

ORGANIC SULFUR CONCENTRATION FOR SEPARATED MACERALS

Variation in organic sulfur concentration can easily be made for maceral fractions separated by density. We have measured several such fractions separated by Dyrkacz (4,5). Results for an Indiana block coal, a high volatile bituminous (PSOC 106) are shown in Fig. 5. There the organic sulfur concentration is plotted as a function of the density of the separated macerals. Approximate boundaries between exinite, vitrinite and inertinite for this coal are shown in the figure. One sees a smooth variation of organic sulfur concentration with density, rising from the inertinites through the vitrinite, peaking at a density near 1.20 g/cc and falling off toward the lighter fractions. The peak at 1.20 corresponds to the maceral-type sporinite.

We have repeated this measurement for four other coals and find the same pattern, the curve being shifted up or down in accordance with the average organic sulfur content (2). We find, as did Raymond earlier (6), that the average sulfur content of the whole coal is about that of vitrinite.

The purpose of this paper is not to emphasize the average organic sulfur concentration of coal or of separated macerals, but to examine the variation of organic sulfur from particle to particle within a particular maceral type. We show this in two steps.

First, measurement of the organic sulfur concentration of the major maceral groups of the Indiana Block Coal (PSOC 106) shows wide variation. The measurements are shown in Fig. 6. One sees wide variation, especially for the exinite.

Second, measurement has been made of the variation of organic sulfur concentration for each of the separated density fractions plotted in Fig. 3. Three of the measurements are shown in Fig. 7 one for each of the major maceral groups. The range of sulfur concentration for the inertinite and vitrinite macerals of density 1.42 g/cc and 1.30 g/cc is again small. But for the fraction at 1.18 g/cc (sporinite) the range is still enormous. Is this a result of maceral impurity, or do pure macerals of the exinites have an intrinsic variation of sulfur content which is very broad?

To make sure that this pattern was not peculiar to coals separated by this gravity-centrifuge process, we have made measurements in situ for 4 macerals of an Illinois #5 coal (7). Those measurements are plotted in Fig. 8, where they are compared to measurements on separated macerals of an Illinois #5 coal. The agreement is satisfactory.

DISTRIBUTION OF ORGANIC SULFUR IN FINELY SEPARATED MACERALS

A laboratory for separating coals into submaceral types by the density gradient method has been established by Professor Crelling at SIU. By pushing the techniques of Dyrkacz to the extreme, he can prepare powdered macerals of even higher purity. He has supplied us with specimens from a bituminous coal #SIU 647 J, an Indiana paper coal. We have measured the organic sulfur content of four of those specimens and show the distributions in Fig. 9.

The organic sulfur content of specimen #1, a cutinite, is a narrow distribution with an average value of about 0.45 wt%, Fig. 9a. The distribution is a single mode. That of specimen #2, also a cutinite with a somewhat lower density, is also a single mode except for 4 isolated points at a much higher organic sulfur concentration, Fig. 9b. Including all points, the average organic sulfur concentration is 0.57 wt%, neglecting the 4 highest points it is about 0.49. It is possible that specimen #1 has a few macerals of another subtype with a higher organic sulfur concentration.

That same trend continues for maceral type #3, a sporinite with a specific gravity about 1.16. One hundred measurements were made for this coal, yielding a bimodal distribution shown in Fig. 9c. It would appear that two maceral subtypes may be present, one with an organic sulfur content near 0.4 wt%, the other near 1.3 wt%. This same bimodal distribution is shown for the density fraction near 1.21, near the edge of the vitrinites, Fig. 9d. A maceral type with organic sulfur content near 0.40 must again be mixed with a maceral with organic sulfur content slightly above 1.0.

These measurements seem to show that macerals separated on a density basis may not be "pure". Thus the broad ranges of data in Figs. 4 and 5 may demonstrate that macerals separated by density techniques may contain two or more submaceral fractions. If one considers the data of Figs. 9c and 9d, the values for the individual modes among this bimodal distribution show a variation of not more than $\pm 20\%$, a value not much different from the variations seen in Fig. 1 for the in-situ macerals, which are assuredly a more pure type, at least locally.

Chlorine Distribution in Coal

The Indiana bituminous coal, PSQC 106, also contains chlorine. We have measured the spatial variation of chlorine in the separated macerals; measurements are shown in Fig. 10. The average chlorine content of this coal is relatively small, about 0.35 wt%. In vitrinite and inertinite the range is relatively small, from about 0.15 to about 0.55 wt%. For the exinites again, the chlorine content is much larger on the average and the spread is much higher, nearly a factor of 10. We have not measured the chlorine distribution in the macerals separated on a finer scale, but it would be easily feasible.

Organic Iron in Coal

We occasionally observe x-ray lines for iron in regions of the foil in which these are not observable precipitates, nor x-ray lines of any other element. We have concluded that these x-rays must show the presence of organic iron. An example is shown for Illinois #5 coal in Fig. 11. The quantity is quite small, less than 0.1 wt%. No variation among the three

major maceral groups was observed. Of course, one always worries that fine oxide particles may be present; but they must be less than perhaps 3 nm in size or we could detect their presence.

SUMMARY

The TEM method for measuring organic sulfur concentration is most valuable when its fine scale spatial resolution can be utilized. We have demonstrated that the variation of organic sulfur is about $\pm 10\%$ of the average when measured over distances separated by 1 μ m. The technique also has value in showing the organic sulfur variation in minute particles of separated macerals. Apparently, it is very difficult using density techniques to obtain pure maceral types.

Acknowledgement: We acknowledge support of the Division of Materials Research, DOE, under contract DE-AC02-76-ER1198. We thank Professor Crelling, SIU, for specimen materials. Support for one of us (M. Buckentin) also came from the State of Illinois through the Center for Research on Sulfur in Coal.

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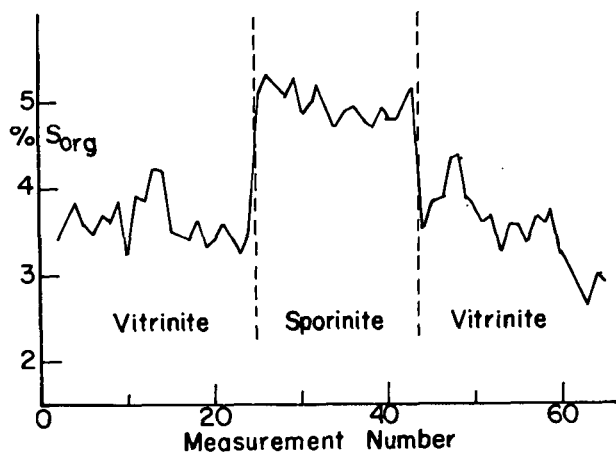


Fig. 1. Organic sulfur trace across a soorinite maceral embedded in vitrinite. Illinois #5.

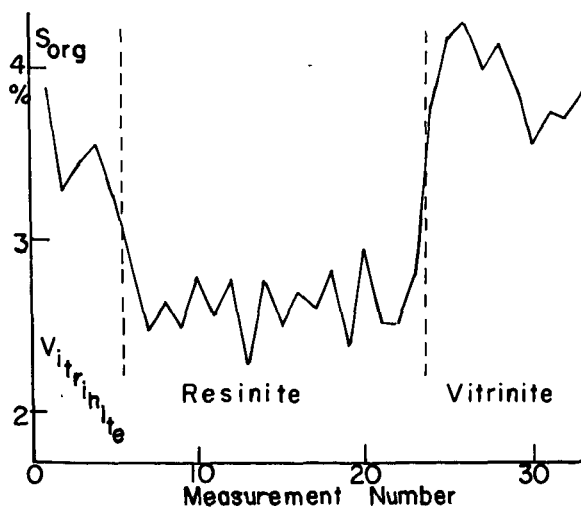


Fig. 2. Organic sulfur trace across a resinite maceral embedded in vitrinite. Illinois #6.

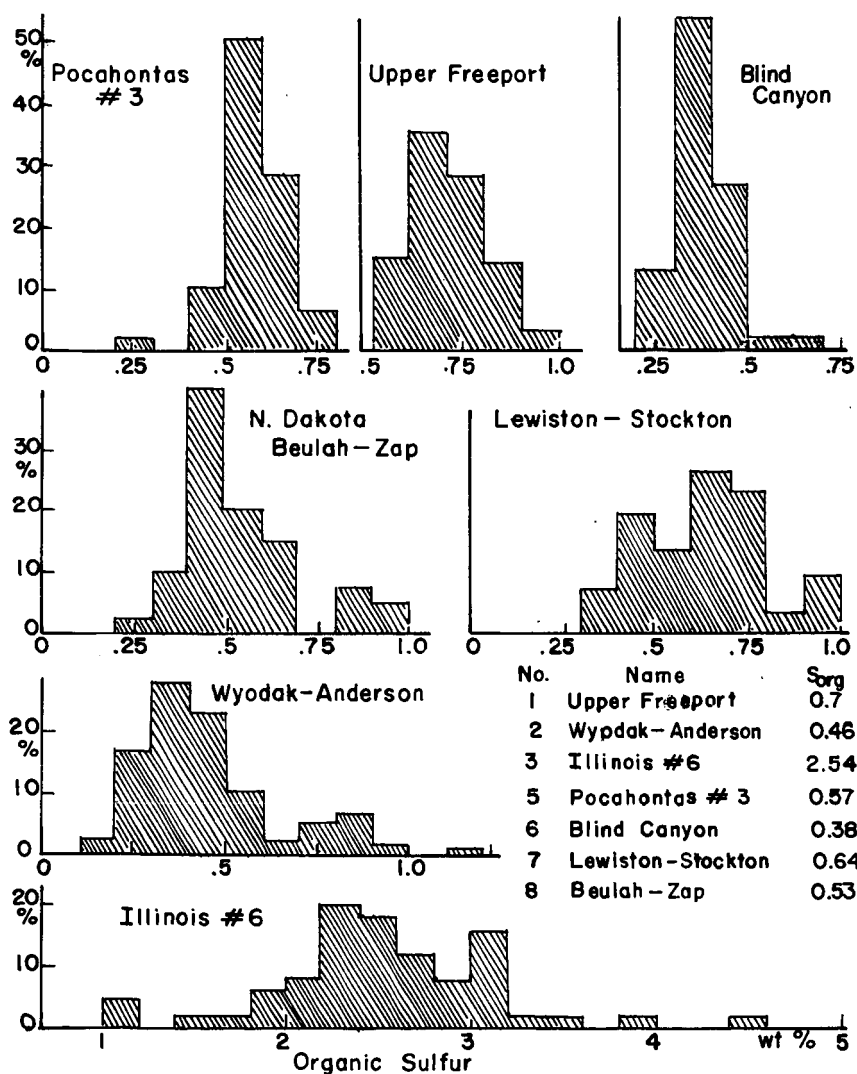


Fig. 3. Distribution of organic sulfur in seven whole coals from the Premium Coal Bank. The inset Table gives the average organic sulfur concentration for each coal.

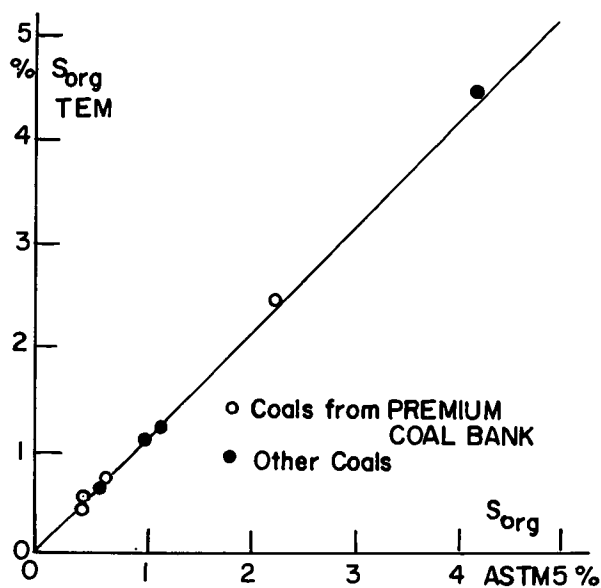


Fig. 4. Comparison of organic sulfur concentration measured by the TEM method and by the ASTM method.

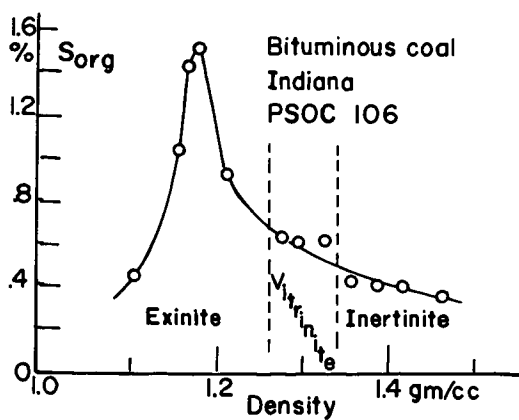


Fig. 5. Variation of organic sulfur for macerals separated by density. Indiana Block coal.

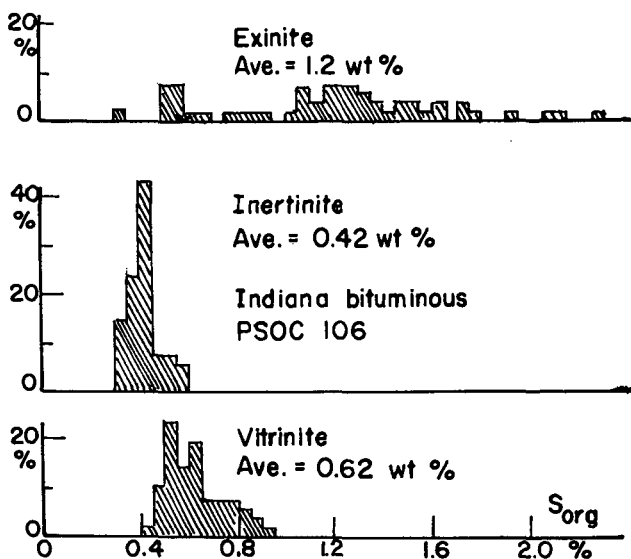


Fig. 6. Distribution of organic sulfur for the major maceral types.

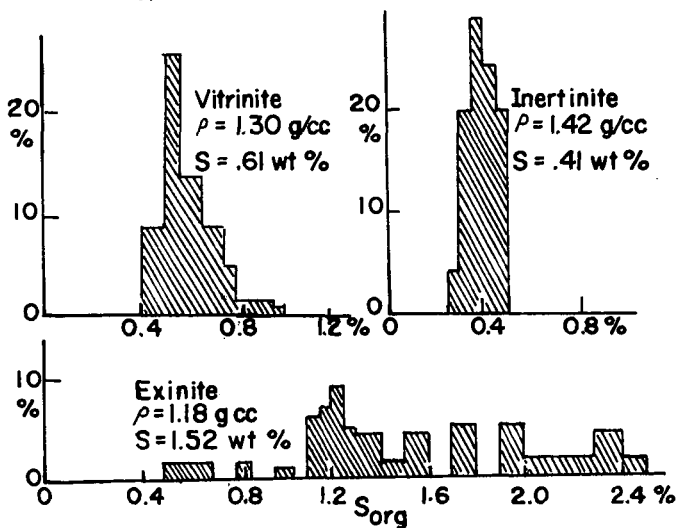


Fig. 7. Distribution of organic sulfur for 3 specific density splits, see Ref. 2 for distribution of other splits.

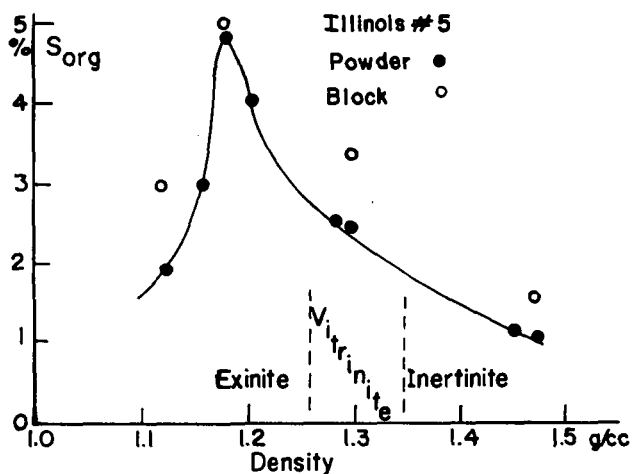


Fig. 8. Comparison of organic sulfur content of separated and in situ macerals.

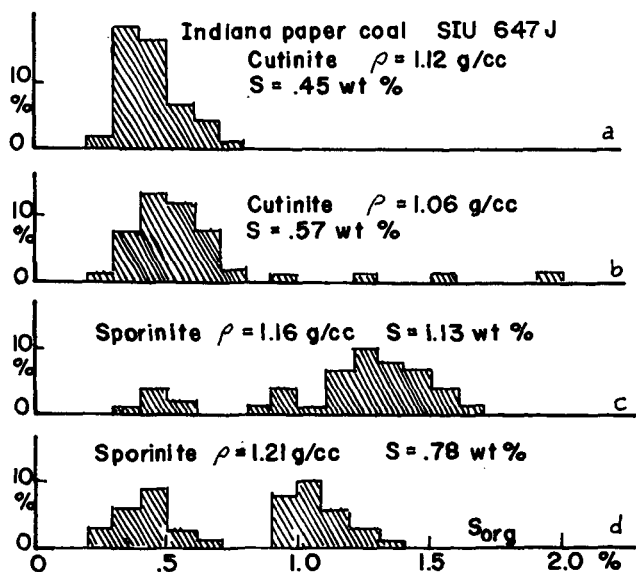


Fig. 9. Distribution of organic sulfur in fine density splits of an exinite.

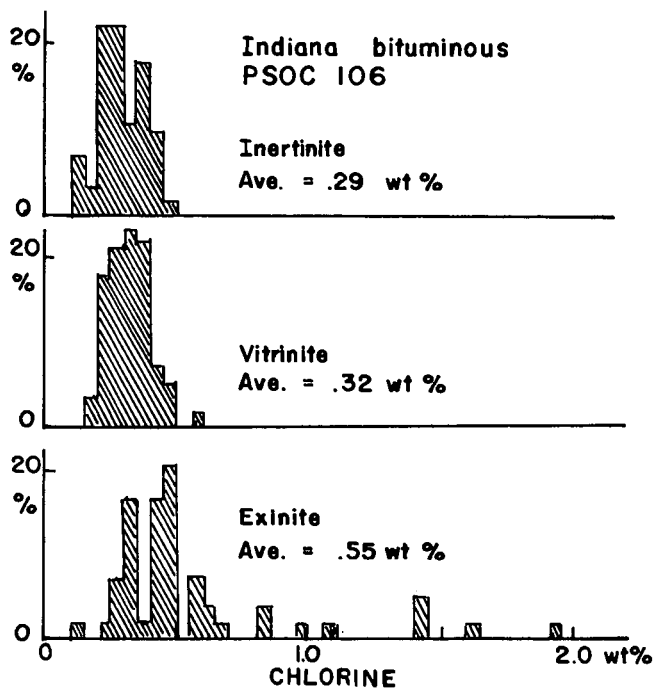


Fig. 10. Distribution of chlorine content of a bituminous coal as a function of maceral type.

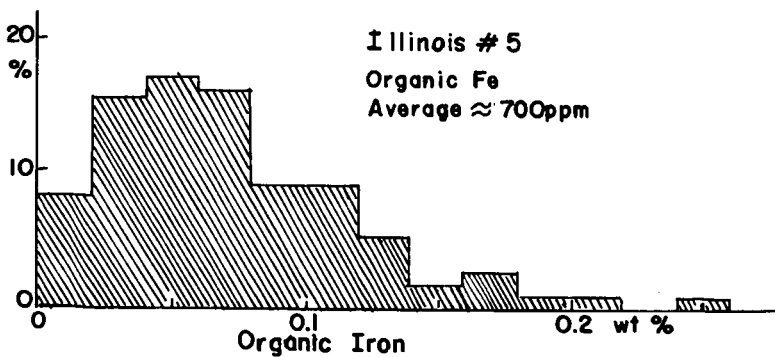


Fig. 11. Distribution of organic iron in a specimen of Illinois #5.

AN ISOTOPE DILUTION STUDY OF EXCHANGEABLE
OXYGEN IN PREMIUM COAL SAMPLES

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The analysis of the moisture content of coals has been the subject of a number of extensive discussions (1-3). Interest in the determination of water in coal is a result of both its importance in commerce and its influence on the elemental analysis of the organic portion of the coal. Although simple weight loss methods, such as ASTM 3173, are the accepted methods for the analysis of moisture in coal, it is well documented that these methods are not without error, especially in low-rank coals. A question of importance is, How much of the water of combustion determined by classical combustion analysis of the coal was present in the "dry" coal as water and is not a combustion product? This water, if present in "dry" coal, can introduce a significant error into the organic elemental analysis. For example, 1% water present in a dry Illinois #6 coal and mistakenly identified as a product of combustion would introduce an error of ~3% in the hydrogen analysis and ~10% in the oxygen analysis. The 3% error in the hydrogen analysis translates into an error of 3 H/100 C for the Illinois No. 6 coal.

Our particular concern regarding the accurate determination of water stems from an interest in the chemistry of hydrogen during direct coal liquefaction. In such systems the change in organic hydrogen across a reactor will often be in the range of 5 H/100 C. If errors due to the unknown amount of moisture in coal are ± 3 H/100 C, a problem exists. If we cannot have confidence in our ability to determine the change in organic elemental composition across a reactor, we cannot, with confidence, discuss the chemistry occurring in that reactor.

The investigation of coal structure can also be complicated by inadequate analysis of the water in the coal. Drying procedures for moisture determination may cause substantial structural changes and, if done in the presence of oxygen, may also induce significant oxidation. The problem of structural collapse on drying is more acute for studies of lower rank coals. Study of the dependence of coal structure on moisture content would be aided by improved methods to measure the nature and amount of water in whole coals.

A difficulty with improving the ability to quantitate water in coal is that truly independent methods do not always exist. The "true" value of any analytical parameter is always easier to determine if totally independent

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

methods exist to determine that parameter. This paper describes the possibility of using a simple isotope dilution technique to determine the water content of coal and presents a comparison of these isotope dilution measurements with classical results for the set of Argonne coals from the premium coal sample program (4).

Isotope dilution is a widely used analytical method and has been applied to the analysis of water in matrices as diverse as chicken fat (4), living humans (5), and coal (6). Virtually all of these applications involved the use of deuterium as the diluted isotope. This poses some problems if the sample contains a significant amount of exchangeable organic hydrogen and one is interested in discriminating exchangeable organic hydrogen from water. This is a potential problem in the coal system. To avoid this potential problem ^{18}O was used as the diluted isotope in this work.

Experimental

The isotope dilution experiment, as applied in this study, involves equilibration of a fixed amount of labeled water with a known amount of coal. If it can be established that complete equilibration has been achieved and if proper allowance is made for isotopic impurities and contributions from the apparatus, the isotope ratio of the final equilibrated system directly measures the exchangeable isotope reservoir in the coal. Further work can then be directed to determining what species compose the exchangeable oxygen reservoir.

The equilibration of the coal with labeled water is accomplished by placing a weighed amount of coal (20-300 mg) in a thin-walled Pyrex tube, adding 5 μL of H_2^{18}O , and using a torch to seal the equilibration tube. The premium coals used were the 100-mesh samples, and all equilibration tubes were filled and sealed within 15 minutes of opening the ampoule. The H_2^{18}O was 90% enriched and was obtained from Mound Laboratories. Before sealing, a small amount of dry $\text{CO}_2(\text{g})$ is added to each equilibration tube as a probe molecule to facilitate mass spectrometric analysis of the isotope ratio. Before analysis, the sealed tubes are equilibrated at 100°C for 16 hours. Measurement of the equilibration rate of coal samples using this experimental approach established that at 100°C , 16 hours was sufficient to guarantee complete equilibration. The isotope ratio measurement on the final system was done by measuring the relative abundances of the isotopic CO_2 species (C^{16}O_2 , $\text{C}^{16}\text{O}^{18}\text{O}$, and C^{18}O_2) using a CEC 103 mass spectrometer. Stable isotope geochemists routinely use CO_2 to measure the oxygen isotopic composition of water samples (7). Distilled water was used for calibration.

Results and Discussion

Determination of the size of the exchangeable oxygen reservoir in the premium coals was accomplished by plotting the observed $^{16}\text{O}/^{18}\text{O}$ isotope ratio against the sample size. Since the amounts of labeled water, CO_2 , and any exchangeable oxygen associated with the sample vessel are held constant, the change in isotope ratio with sample size should be a function of only the size of the exchangeable oxygen reservoir in the coal. The isotope dilution data obtained for the eight currently available premium coals are

presented in Figure 1. The slopes of the plots shown in Figure 1 are simply proportional to the size of the exchangeable oxygen reservoir in each of the premium coals.

Conversion of the raw data to "water" content and comparison of these results with the best currently available moisture analyses on the premium coals is shown in Table 1. The assumption that is made is that the exchangeable oxygen reservoir is all present as water. These results indicate good agreement between the isotope dilution measurement and the classical moisture measurements on this set of samples. There appears to be a small systematic positive difference between the isotope dilution and the weight loss results. This difference is believed to be outside our experimental error. Before the set of premium coals was analyzed, a number of ground coals being used in process-related studies had been analyzed by this method. For these samples, which had not been handled with the care lavished on the premium samples, discrepancies between the isotope dilution measurements and the classical weight loss analyses were significantly greater. This is illustrated by the last two entries in Table 1. At this point in the development of the isotope dilution technique, a definitive explanation of the larger discrepancies between isotope dilution and weight loss results for the non-premium samples would be premature. A potential source of these differences could be mild oxidation and structural changes in the non-premium samples, resulting in water being more strongly bound and thus incompletely measured in the weight loss analyses. Further work is needed to clarify the reasons for these differences.

The data presented indicate that an isotope dilution approach is capable of reproducibly measuring the size of an exchangeable oxygen reservoir in coal. To determine what oxygen is included in the exchangeable oxygen reservoir, the size of the reservoir was determined for a variety of model systems, including clay minerals, calcite, gypsum, inorganic hydrates, phenolics, carboxylic acids, carboxylate salts, carboxylate salt hydrates, and accepted geochemical standards. The discussion of all these results exceeds the scope of this preprint; however, the preliminary conclusion is that under the conditions described in this work, the exchangeable oxygen reservoir includes most strongly bound hydrate water in both organic and inorganic systems and does not include any organic oxygen in compounds that are stable under the equilibration conditions.

Conclusions

Equilibrium isotope exchange for the investigation of oxygen in coal appears to have promise as a tool for determination of the "true" water content of coals. Its applicability appears to extend across the rank scale. The technique measures the size of the exchangeable oxygen reservoir under very mild conditions without removing the water from the coal, thus avoiding structural changes that could complicate the analysis. A more comprehensive discussion of the results on a variety of systems is currently being prepared. Preliminary results indicate that it may provide a simple, reliable, and totally independent method for the measurement of coal water content. Comparison of this method with classical weight loss methods may provide a significant improvement in our ability to measure the "true" water content of coal and thus the "true" organic hydrogen and oxygen contents as well.

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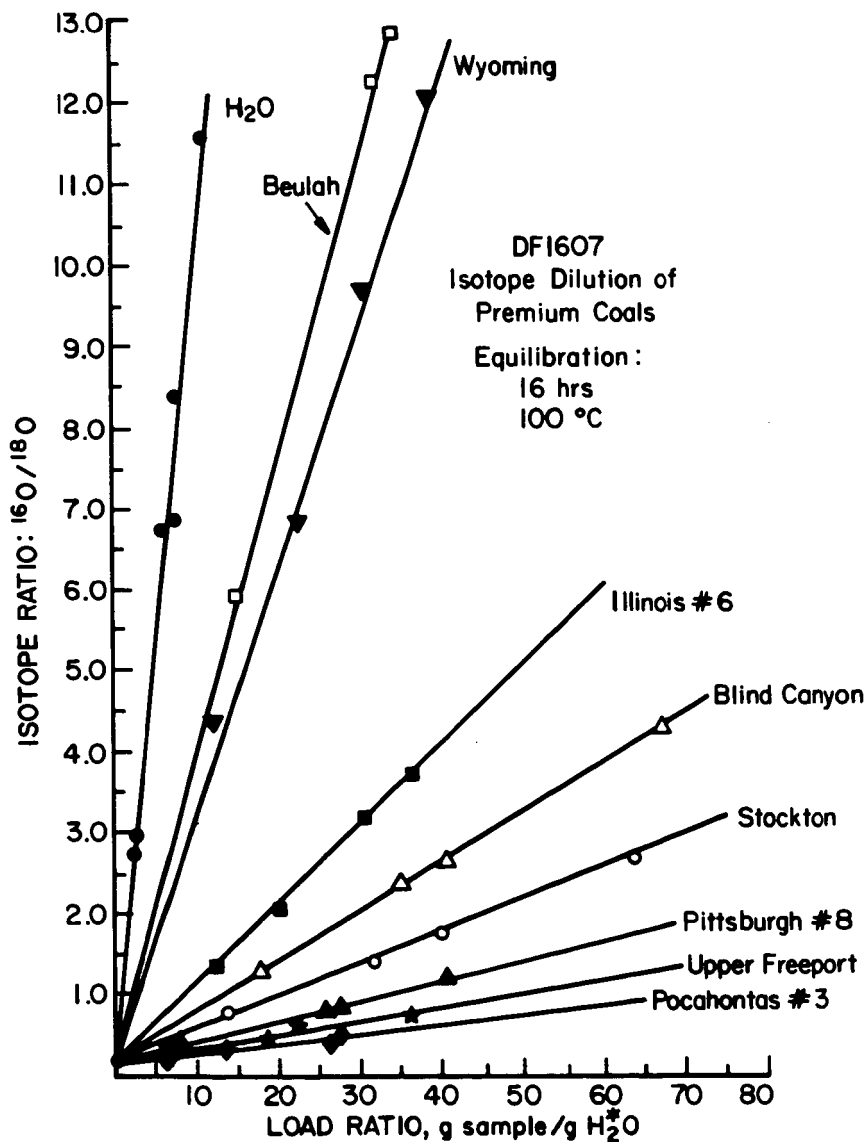


Figure 1. Isotope Dilution Analysis of Premium Coals.

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TABLE 1.
"MOISTURE" IN COALS
(Exchangeable Oxygen Reservoir)

Coal	Isotope Dilution Analysis (Wt%)	Standard Method (Wt%)*
Beulah-Zap	34.4	32.8
Wyodak	30.0	28.84
Illinois #6	9.6	8.8
Blind Canyon	5.9	4.7
Stockton	3.9	2.6
Pittsburgh #8	2.5	1.8
Upper Freeport	1.5	0.83
Pocahontas	1.0	0.66
Clovis Point	27.6	20.4
River King	9.8	7.7

"Premium"
Samples

"Non-Premium"
Samples

*For Premium Samples, Data Obtained from Argonne National Lab.
Non-Premium Samples Were Analyzed by ASTM 3173.

THE APPLICATION OF INVERSE GAS CHROMATOGRAPHY TO COALS AND OXIDIZED COALS

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INTRODUCTION

In two previous papers (1,2) we reported preliminary results concerning the application of Inverse Gas Chromatography (IGC) to coals and air oxidized coals. In this paper we will report on the reproducibility of the IGC technique, its application to other Argonne Premium Coals, and compare the results with those obtained with pyrolysis mass spectroscopy. The objective of this study is to provide detailed information concerning the possible non-oxidative changes in the chemical and physical structures of the Argonne Premium Coal Samples (APCS) during long term storage. Inverse gas chromatography is just one of the techniques being utilized in meeting this objective. It is known that subtle changes in coal structure can effect changes in plasticity when a coal is heated. However, the techniques traditionally used to measure plasticity do not yield information which can be used to understand the underlying chemical and physical changes in the coal structure.

Inverse gas chromatography, a technique widely used for studying polymers, is being used to study the transitions that the APCS undergo upon heating. Inverse gas chromatography has been applied to polymers to measure the glass transition temperature, the degree of crystallinity, melting point, thermodynamics of solution, and chemical composition (3-5). Inverse gas chromatography has also been applied to coals in the temperature region less than 85°C to determine the enthalpy of sorption of methane and oxygen on dried coals (6). For methane the enthalpies of sorption ranged from 4.4 to 0.9 Kcal/mole for Czechoslovakian coals between 90.7 and 83.3 percent carbon on a dry ash free basis.

In contrast to classical gas chromatography, inverse chromatography probes the stationary phase, a coal, by determining the retention time of known compounds on it. This transposition of known and unknown in the gas chromatography experiment gives rise to the term "inverse chromatography". Two types of information are provided by the IGC experiment. The slope of a plot of the log of the retention time versus the inverse of the temperature is proportional to the enthalpy of retention for the probe molecule on the coal. This is a thermodynamic measure of strength of the interaction between the probe molecule and the coal. The temperatures at which major changes in slope are observed represent the points where the mechanism of retention has changed significantly, indicating that a significant change in the chemical or physical structure of the coal has occurred.

EXPERIMENTAL

The elemental compositions of the coals used in this study are shown in Table 1. The preparation of the Argonne Premium Coal Samples has been

described by K. Vorres and S. Janikowski (7). The -100 mesh samples were thoroughly mixed with non-porous glass beads (-400 to -60 mesh) to give a mixture approximately 10% coal on a weight basis. A blank experiment utilizing only glass beads yielded an effective slope of 0, indicating that adsorption of methane on the non-porous glass beads was minimal. The six foot by 1/4 inch glass columns were packed with ca. 30 grams of the mixture. All transfers and weighings were performed in a glove box under nitrogen atmosphere.

A diagram of the experimental apparatus is provided in Figure 1. The gas chromatography equipped with a single flame ionization detector could be controlled from an external computer. The injector was a computer controlled Carle gas sampling valve in a thermostated box. Flow control was provided by two flow controllers one with a 0-5 ml/min. element and the second with a 0-60 ml/min. element. The second controller was connected to the injector through a computer controlled solenoid. The experiment was controlled and the data analyzed by an IBM PC computer.

A flow diagram of the IGC experiment is shown in Figure 2. The experiment begins with an initial equilibration period of at least 24 hours, during which the flow rate of the helium carrier gas was cycled between it's chromatographic rate of 1 ml/min. and the higher rate (30 ml/min.). The higher flow rate was used to speed the removal of volatile matter from the column after each temperature increment. The probe, 10% methane in argon, was injected onto the column and it's retention time at the specific temperature determined. In the experiment duplicate chromatograms were obtained in four degree increments between 50 and 450°C. After each temperature increment the baseline signal was determined and compared to the baseline at the previous temperature. If it had increased more than 10% the solenoid isolating the second flow controller was opened increasing the rate at which the coal volatile matter was purged from the column. Even with increasing the flow rate, an IGC experiment could take up to a month to perform. The injector was held at 100°C and the detector at 400°C.

The Pyrolysis Mass Spectrometry (PyMS) technique has been described previously (8). Briefly the coal sample was placed on a platinum 5% rhodium mesh on the end of a probe as a slurry. After the solvent had evaporated the probe was inserted into the mass spectrometer and positioned within 5 mm. of the source. The probe which had been previously calibrated with an infrared thermometer was computer controlled to give a temperature profile beginning at 100°C and increasing at 50°C/min. to 800°C. This technique results in the relatively slow vacuum pyrolysis of the coal sample.

RESULTS AND DISCUSSION

The results from the IGC experiment on Upper Freeport Coal (APCS #1) are presented in Figure 3. The plot of the Log of the retention time versus the inverse of the temperature in degrees Kelvin is divided into three general regions based on the slope of the curve. The first major transition is bounded by the significant change in slope normally found between 100 and 120°C. We believe that this transition is caused by the loss of water from the pore structure of the coal. This change in slope indicates that the way the methane probe molecule interacts with the wet coal, or the mechanism of

retention, is different enough from that of the dry coal to produce the observed deviation in curve. The intermediate temperature region (ca. 115°C to ca. 350°C) is a long region in which a relatively constant slope is observed. This indicates that the mechanism of retention for the methane probe molecule does not change significantly. However, above 200°C a large number of small transitions are encountered which do not result in a major deviation from the prevailing slope. We believe that these are due to the loss of volatile matter occluded within the coal structure. The loss of relatively minor amounts of material should result in small deviations in retention time, which are observed but would not be expected to modify the overall mechanism of retention significantly. In region 3 (>350°C) there is a marked change in the slope indicating a major change in the mechanism by which the methane probe is retained by the coal in the IGC experiment. This corresponds to the temperature region in which Giesler Plastimeter results indicate that the coal is in the fluid state.

The reproducibility of the IGC technique is shown in Figure 4, where the results from duplicate experiments on Illinois No. 6 (APCS #3) are presented. As can easily be seen, the results from the two experiments are very similar. Not only do the major transitions occur at the same temperatures, but many of the minor transitions are reproduced as well. The two curves appear to be most dissimilar in the low temperature region. This is where we believe that changes in retention are dominated by water in the coal. Thus the results should be most sensitive to variation in sample handling. The minor transitions in the intermediate temperature region (120-300°C) are reproduced very accurately. Both curves show minor transitions around 190, 230 and 285°C. The temperature of the major transition appears to be similar for the two experiments. An exact assignment of the temperature of this transition in experiment two is impossible due to a problem with the data system, which resulted in the loss of data between 300 and 326°C. In the higher temperature region (>326) reproducible transitions occurred near 380 and 420°C. The enthalpies of sorption were very similar and well within the calculated precision of the data as can be seen in Table 2.

The variation in the temperature at which the major transition peak occurs for each of the coals studied are plotted versus percent carbon in Figure 5. This peak marks the start of the high temperature region in each of the experiments. This transition can be seen in Figure 3 just above 350°C for Upper Freeport coal, in Figure 4, just below 326°C for Illinois No. 6, and at 370°C in Pocahontas coal in Figure 7. The limited number of samples studied precludes stating that a correlation exists, however one is safe in assuming that a trend is indicated.

The enthalpy of sorption for each of the coals studied plotted versus carbon content is presented in Figure 6. The data was derived from the regression of the IGC data above the temperature of the major transition. As with the temperature of the major transition a trend is definitely indicated. However, several of the enthalpies are unrealistically high. This is probably due to changes in column void volume in this region which would significantly affect the calculated values.

Figure 7 compares the results from the IGC experiment with those obtained from PyMS for Pocahontas coal. Although the pyrolysis was started at 100°C, the total ion current signal below 208°C was dominated by an internal standard

added to the coal. Other experiments indicate that very little material of molecular mass >31 is released below this temperature. Above this temperature minor transitions in the IGC curve become more numerous. This indicates that these minor transitions in the IGC are indicative of the loss of volatile material. The maximum in the Total Ion Current (TIC) is observed at a temperature very close to that of the major transition in the IGC experiment. At temperatures above the major transition the TIC curve indicates that the release of volatile material begins to decrease significantly.

Overall, IGC appears to be a very reproducible method for following the chemical and physical changes that occur when coals are heated in an inert atmosphere. Differences in both the temperature of the transitions and enthalpies of sorption can be observed for coals of various rank. Pyrolysis Mass Spectrometry results indicate that the minor transitions observed in the intermediate temperature region are due to the loss of volatile matter from the coal.

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TABLE 1. Composition of Coals Studied.

Coal	% C (dmmf)	Empirical Formula
Upper Freeport mv Bituminous (APCS #1)	87.1	$C_{100}H_{75}N_{1.5}S_{0.3}O_{2.6}$
Illinois No. 6 hvC Bituminous (APCS #3)	77.8	$C_{100}H_{88}N_{0.6}S_{0.5}O_{3.7}$
Pocahontas 1v Bituminous (APCS #5)	89.6	$C_{100}H_{63}N_{1.2}S_{0.2}O_{3.3}$
Bruceton hvA Bituminous	82.3	$C_{100}H_{78}N_{1.6}S_{0.3}O_{9.3}$

TABLE 2. Enthalpies of Sorption in the Three Temperature Regions.

Coal	50-100°C	100-300°C	350-400°C
	Very Low Temperature Region†	Low Temperature Region†	High Temperature Region†
Upper Freeport mv	2.9 ± 0.5	$1.93 \pm .07$	12.5 ± 0.4
Pocahontas 1v	--- *	$2.01 \pm .04$	14.8 ± 0.4
Bruceton hvA	1.6 ± 0.2	$1.96 \pm .04$	7.7 ± 0.4
Illinois No. 6 (1)	4.0 ± 0.3	$2.00 \pm .16$	4.9 ± 0.5
Illinois No. 6 (2)	4.3 ± 0.3	$1.90 \pm .15$	5.1 ± 0.5

†Temperatures indicated are approximate, the actual boundaries were determined by the temperature of the actual transitions in the specific experiment.

*Pocahontas coal exhibited a negative slope in this region for some unknown reason.

Figure 1. Experimental apparatus for inverse gas chromatography experiment.

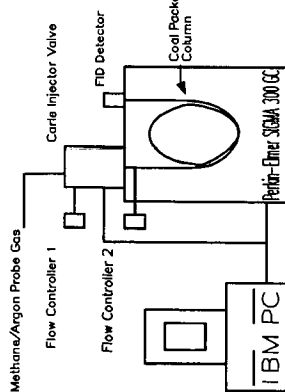


Figure 2. Flow Diagram of inverse gas chromatography Experiment.

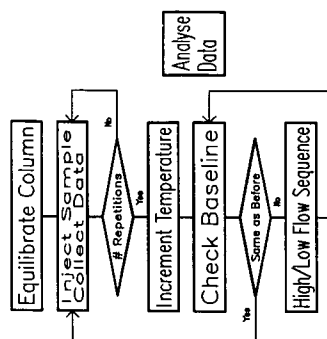


Figure 3. Plot of the log of the retention volume versus the inverse of temperature for Upper Freeport coal (APCS No. 1).

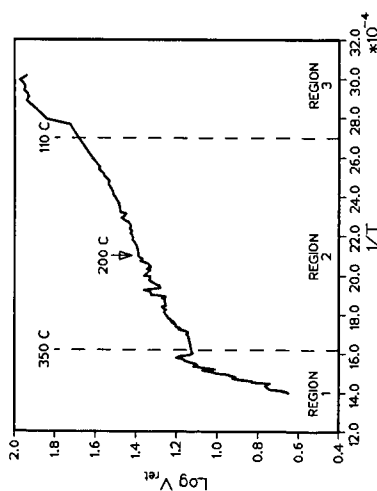


Figure 4. Comparison of IGC experiments on Illinois No. 6 coal (APCS No. 3).

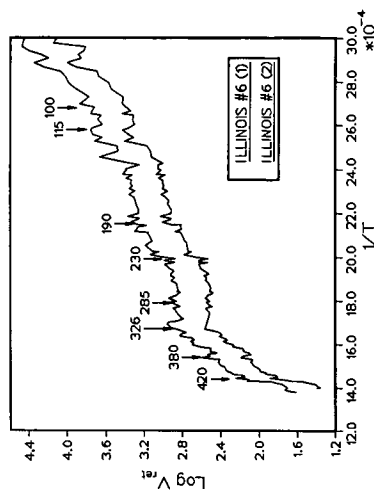


Figure 5. Variation in the temperature for the start of the major transition versus carbon content (dmmf) for APCs#3, Bruesdon, APCs#11, and APCs#5 coals.

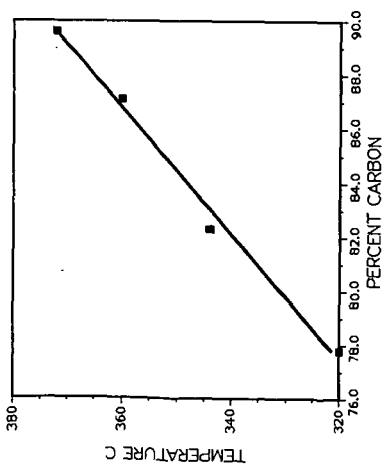


Figure 6. Variation in the enthalpy for the high temperature region (C50-450 °C) versus carbon content (dmmf) for APCs#3, Bruesdon, APCs#11, and APCs#5 coals.

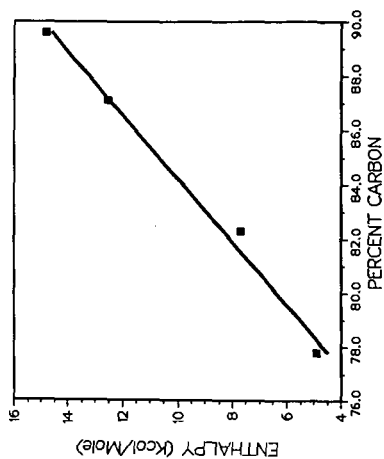
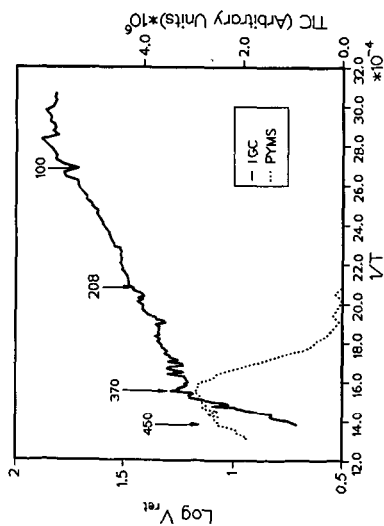


Figure 7. Comparison of IGC and pyrolysis high resolution mass spectrometry data for Pocahontas IV bituminous coal (APCS No. 5).



¹³C NMR Structural Determination of the Coals in the Premium Coal Sample Bank

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Introduction

Solid state ¹³C cross polarization (CP) magic angle spinning (MAS) NMR experiments have become very useful for the study of the structure of coal and other fossil fuels (1, 2). Solid state NMR techniques have the advantage over liquid NMR methods because the whole solid coal can be analyzed in a nondestructive manner and no assumption need be made that the soluble portion represents the whole organic portion of the coal. From CP/MAS experiments twelve NMR structural parameters may be determined including the aromaticity, f_a , that give information on the carbon skeletal backbone. The variation of the NMR structural parameters for coals of different rank from lignite to anthracite has been demonstrated (3). The coals in the Premium Coal Sample Bank (PCSB) have been included in the set of coals studied at the Advanced Combustion Engineering Research Center. The NMR data obtained on these coals will be used to provide chemical structural parameters for refinement of the devolatilization sub-model of the PCGC-2 combustion model.

This paper reports the twelve structural parameters for two of the PCSB coals, Pittsburgh #8 (HVB) and Blind Canyon (HVB). These data were derived from integrated intensities in a normal CP/MAS experiment along with a complete set of dipolar dephasing experiments. In addition, the proton spin lattice relaxation times for these coals have been determined. From relaxation experiments on the Pittsburgh #8 coal there is some evidence of heterogeneity between different sample vials of the same standard coal.

Experimental

The coal samples studied were Argonne Premium Coal Bank samples of: Pittsburgh #8, high volatile bituminous, COAL_ID: 401, vials 137,140,157,159 and Blind Canyon Seam, high volatile bituminous, COAL_ID: 601, vial 90. All spectra were taken on a Bruker CXP-100. A single contact of 2.5 ms was employed for all T_1 and dipolar dephasing experiments together with a pulse delay time of 1.0 ms which is greater than $5T_1$'s for both coals. The samples were opened in a nitrogen glove bag, placed in a capped boron nitride rotor, and spun under nitrogen gas except for vials 137 and 159 of the Pittsburgh #8 which were opened in air and then placed immediately in the rotor. All

chemical shielding values are given in ppm with respect to external TMS. The pulse sequence used to measure the proton T_1 indirectly by observing the carbon resonance is described in detail by Axelson (1) and the dipolar dephasing sequence which includes refocusing pulses in both carbon and proton channels has been described by Alemany et. al. (4).

Results and Discussion

Proton Spin Lattice Relaxation

The proton T_1 's are given in Table I for both the aromatic and aliphatic regions of one Blind Canyon vial and for four different vials of the same Pittsburgh #8 coal.

Table I: T_1^H (ms) Values for Two Argonne Coals.

Coal and Vial #	Aliphatic	Aromatic
Pittsburgh #8		
137	192 ± 7	193 ± 6
140	206 ± 9	194 ± 5
157	152 ± 5	140 ± 2
159	151 ± 10	138 ± 5
Blind Canyon		
90	60 ± 3	43 ± 2

\pm = one marginal standard deviation from three parameter fit.

The four different vials of Pittsburgh #8 have T_1^H values that fall into two groups, two with T_1 's of approximately 195 ms and two with values in the 140-150 ms range. To check the reproducibility of the T_1 data, two different experiments were performed on a sample without removing it from the spectrometer. The measured T_1 's were well within one marginal standard deviation (MSD) of each other, implying that the difference in the Pittsburgh #8 is greater than the experimental error. It is postulated that during the physical mixing and grinding of this coal, paramagnetic centers may not have been randomly distributed. The T_1 's measured for both aliphatic and aromatic regions give the same value within two MSD for the Pittsburgh #8 samples demonstrating that spin diffusion is an efficient relaxation mechanism in this sample. For the Blind Canyon sample T_1^H is much shorter than Pittsburgh #8. The T_1 's for the aliphatic and aromatic regions of the spectrum differ by more than three MSD indicating that spin diffusion does not occur throughout the whole sample.

Dipolar Dephasing and Structural Parameters

Under the conditions of the dipolar dephasing experiment the carbon magnetization can be characterized by a decay constant, T_2 , which depends on the strength of the ^1H - ^{13}C dipolar coupling. Characteristic values of T_2 for CH , CH_2 , and CH_3 groups in model compounds and coals have been reported (3, 4, 5, 6). The T_2 decay curve is usually characterized by two time constants: a Gaussian component characterized with a time constant, T_G , for rapidly decaying components (CH and CH_2 groups) and a Lorentzian component with a time constant, T_L , for slowly decaying components (rapidly rotating methyl groups and nonprotonated carbons). An example of the decay curve for the magnetization, $M(t)$, for the aromatic region of Pittsburgh #8 is shown in Figure 1 and was fit to the following equation:

$$M(t) = M_{0L}e^{-t/T_L} + M_{0G}e^{-0.5(t/T_G)^2} \quad 1)$$

where M_{0L} and M_{0G} are the relative amounts of slow and fast decaying carbon magnetization at $t = 0$.

The above equation is applied separately to the decay of the aromatic and aliphatic regions of the spectrum and four parameters (M_{0L} , T_L , M_{0G} , T_G) are determined for each region and are used with integrated intensities, I , over various regions of the spectrum to determine the 12 structural parameters as follows:

$$\begin{aligned} f_a &= (I_{>90} + 2I_{ss})/I_{\text{total}} \\ f_a^C &= I_{>165}/I_{\text{total}} \\ f_{a'} &= f_a - f_a^C \\ f_a^H &= (M_{GO}^{\text{ar}}/M_{\text{total}}^{\text{ar}}) \times f_{a'} \\ f_a^N &= f_{a'} - f_a^H \\ f_a^P &= I_{150-165}/I_{\text{total}} \\ f_a^S &= I_{135-150}/I_{\text{total}} \\ f_a^B &= f_a^N - f_a^S \\ f_{al} &= 1 - f_a \\ f_{al}^H &= (M_{GO}^{\text{al}}/M_{\text{total}}^{\text{al}}) \times f_{al} \\ f_{al}^* &= f_{al} - f_{al}^H \\ f_{al}^O &= I_{50-90}/I_{\text{total}} \end{aligned} \quad 2)$$

where I_{total} is the total integrated intensity of the whole spectrum, I_{ss} is the integrated intensity of the down field spinning sideband and I_{ppm} 's are the integrated intensities over

selected chemical shift ranges in ppm. These structural parameters are listed in Table II for the two coals and the normal CP/MAS spectrum is shown in Figure 2 for Pittsburgh #8 (bottom) and Blind Canyon (top).

Although both of these coals are of the same rank and nearly identical carbon content there are variations in some of the structural parameters. The f_a value for the Pittsburgh #8 is 0.75 while a lower value of 0.64 is found for the Blind Canyon coal indicating that more of the carbon is sp^2 -hybridized in the Pittsburgh #8. From the elemental analysis data (7) the atomic H/C ratio is 0.79 for the Pittsburgh #8 and 0.91 for the Blind Canyon samples. The higher H/C ratio for the Blind Canyon coal is not surprising since this coal contains approximately 15% liptinite which is highly aliphatic and thus hydrogen rich. Using H/C data together with the f_{al}^H and f_a^H values for the two coals one notes that the H/C ratios for the aromatic and aliphatic regions are 0.37 and 2.0 for Pittsburgh #8 and 0.34 and 1.97 for Blind Canyon. This would seem to indicate that both the aliphatic and aromatic regions are quite similar but, as can be seen from the spectra, the aliphatic regions of the two coals appear to be significantly different. If it is assumed that the parameter f_{al}^* represents only methyl groups and the H/C ratio of the aliphatic region appropriately corrected, then the H/C ratio of the remaining aliphatic region for the two coals is 1.3 for Pittsburgh #8 and 1.7 for Blind Canyon. These differences can now be used to rationalize the marked spectral differences observed in the aliphatic regions of the two coals. The aliphatic structure of the Pittsburgh #8 is probably more highly branched, having more CH groups and a lower H/C ratio than the Blind Canyon coal which probably has more straight chains with CH_2 groups or nonsubstituted tetralin-type structures contributing to the higher aliphatic H/C ratio.

This work demonstrates that solid state NMR techniques can be used to distinguish structural differences in coals that are of the same rank as well as determining structural differences in coals of varying ranks. Similar data will be taken on all of the PCSB coals. This data will be used to assess those structural features that make major contributions to devolatilization behavior of the coals in the combustion processes.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation's Advanced Combustion Engineering Research Center, Contract No. CDR-8522618.

Table II: Structural Distribution of Argonne Coals.

COAL	f_a	$f_{a'}$	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
PITTSBURGH #8 (HVB)	.75	.75	.00	.28	.47	.06	.17	.30	.25	.14	.11	.03
BLIND CANYON (HVB)	.65	.64	.01	.22	.42	.07	.15	.27	.35	.27	.08	.04

f_a = Fraction of total carbon that is sp^2 -hybridized.

$f_{a'}$ = Fraction of total carbon that is sp^2 -hybridized and in an aromatic ring.

f_a^C = Fraction of total carbon that is carbonyl - $\delta > 165$ ppm.

f_a^H = Fraction of total carbon that is sp^2 -hybridized and protonated.

f_a^N = Fraction of total carbon that is sp^2 -hybridized and nonprotonated.

f_a^P = Fraction of total carbon that is phenolic or phenolic ether - $\delta = 150 - 165$ ppm.

f_a^S = Fraction of total carbon that is sp^2 -hybridized and alkylated - $\delta = 135 - 150$ ppm.

f_a^B = Fraction of total carbon that is sp^2 -hybridized and at a bridgehead position.

f_{al} = Fraction of total carbon that is sp^3 -hybridized.

f_{al}^H = Fraction of total carbon that is sp^3 -hybridized and CH or CH_2 .

f_{al}^* = Fraction of total carbon that is sp^3 -hybridized and CH_3 or nonprotonated.

f_{al}^O = Fraction of total carbon that is sp^3 -hybridized and bonded to oxygen - $\delta = 50-90$ ppm.

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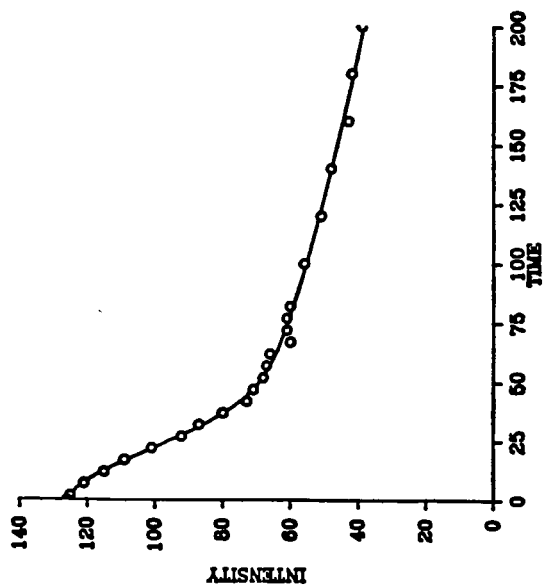


Figure 1. Dipolar dephasing decay curve for the aromatic carbons of Pittsburgh #8. Times are in μ s.

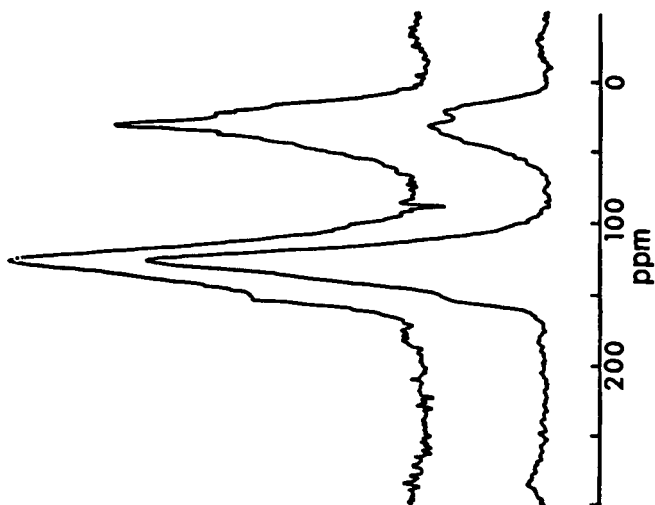


Figure 2. CP/MAS spectra of Blind Canyon (top) and Pittsburgh #8 (bottom).

MULTINUCLEAR NMR CHARACTERIZATION OF THE LAYER SILICATES IN ARGONNE PREMIUM COALS AND MODEL SYSTEMS

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INTRODUCTION

A variety of pulse sequences have been used to obtain solid-state aluminum-27 and silicon-29 nuclear magnetic resonance (NMR) spectra on the mineral matter in Argonne Premium Coals. The aim of this research investigation is two-fold; to improve our knowledge of minerals found in coals and to elucidate the possible roles of layer silicates in coal formation. To facilitate the latter objective, layer silicates that are intimate with the carbonaceous portion and present during coalification must be identified. Nuclear magnetic resonance should provide valuable information because it is sensitive to all mineral particles independent of their size and it is a direct characterization method, thus does not require any modification of the coals.

In the present study, NMR has been applied to the entire suite of Argonne Premium Coals before and after separation of the detrital mineral particles by sink-float separation (1). Preliminary results are presented for the direct characterization of the minerals more intimately associated with the organic portion of these coals.

EXPERIMENTAL

NMR Spectroscopy. The silicon-29 cross-polarization (CP) (2) and spin-echo (3) spectra employing magic-angle sample-spinning (MAS) (4) were recorded at 19.89 MHz on a Bruker Instruments spectrometer, model CXP-100. The CP/MAS spectra were recorded with contact times varying from .1 to 20 ms, a 2-second repetition time and with proton-decoupling during acquisition. The Hartman-Hahn matching condition was set with pure kaolinite spinning at about 3.5 kHz; all CP/MAS spectra were recorded at the same speed as the standard. The spin-echo spectra were recorded with and without proton decoupling during acquisition and with a repetition time of .2 to 2 seconds depending on T_1 . The total time required to obtain the silicon-29 spectra varied from an hour to 15 hours for CP/MAS spectra and 2 to 50 hours for spin-echo spectra. The aluminum-27 MAS, variable angle sample spinning (VAS) (5) and static spectra were recorded with a 45° pulse (2.5 μ s pulse width) at 52.2 MHz on a Nicolet Magnetics spectrometer, model NTC-200. The aluminum-27 spectra required an hour to 15 hours for data acquisition. Chemical shifts are referenced to TMS for silicon-29 and a 1 M aqueous solution of $AlCl_3$ for aluminum-27.

Preparation of Mineral Concentrates by Sink-Float Separation. A typical procedure to obtain concentrates of minerals was to suspend -100 mesh Argonne Premium Coal in a 1.42 g/cm solution (1 g coal/10 mLs) by ultrasonification. The coal slurries were centrifuged for 30 to 90 minutes to allow for the density separation. The raw coal was clearly separated into a black,

carbonaceous upper portion (low density) and a grayish mineral portion on the bottom. These two portions could be readily separated with minimal mixing by decantation. The two portions were separately washed with water and ethanol to remove the CsCl and Brij-35 and were subsequently dried in a vacuum oven at room temperature.

RESULTS AND DISCUSSION

Several commercially available layer silicates and their chemically modified variants were analyzed to determine the optimum spectral parameters required for their observation. Methods were also developed to distinguish between the layer silicates present and to find ways to overcome the problems of poor sensitivity. In silicon-29 NMR experiments, cross-polarization can be used to take advantage of the dipolar coupling to protons thereby enhancing the signal of the dilute nuclear spin system. The appropriate mix time depends on the rate of polarization transfer, or the effective silicon-proton internuclear distance, and the lifetime of the proton magnetization. The results of these experiments on all Argonne Premium coals showed that using a mix time of approximately 5 ms selectively enhances the sharp kaolinite resonance at -92.5 ppm (compare Figs 1a and 1b). This was a surprising result since other silicates are expected to have structures with silicon-proton distances similar to kaolinite. However, it allowed the unambiguous identification of kaolinite in all of the Argonne Premium Coals even when a small amount of kaolinite was found in the presence of a large number of other minerals. The silicon-29 spin-echo NMR spectrum, in addition to having a resonance from kaolinite (see Fig. 1a) also exhibits a resonance at -108 ppm from quartz, as well as resonances from several other silicon sites (some minerals may have several resonances due to crystallographic inequivalence) in the region from -75 to -95 ppm. Silicon-29 resonances in the latter region are typical of montmorillonite or illite clays having SiO_4 structures with two or three of their next nearest neighbors as silicon and the remaining next nearest neighbors as aluminum and/or hydrogen. The kaolinite resonance at -92.5 ppm was narrowed from 3 ppm to 1 ppm when proton decoupling was employed. However, no significant change in linewidth was observed for the other resonances which prevented further identification of other layer silicates. A proton decoupling field of 48 kHz was employed and should have been of sufficient magnitude to decouple all protons from silicon. Thus, other line-broadening mechanisms, for example, bulk susceptibility anisotropy effects arising from noncrystallinity, must dominate the resonances of the other minerals. It should be pointed out that the silicon-29 NMR spectral parameters were selected to discriminate against quartz-like minerals (although quartz resonances do appear in some spectra at -108 ppm, Figs. 1a and 1c) in order to maximize conditions for observation of the layer silicates.

The solid-state aluminum-27 NMR spectra of the Argonne Premium Coals show that a greater proportion of their aluminum is found in octahedral environments (Table 1), some of which is due to kaolinite, and differing amounts of tetrahedral aluminum. The aluminum-27 spectrum of Illinois #6 bituminous coal (APCS #3) shown in Fig. 2a exhibits tetrahedral resonances in the region centered at 65 ppm and octahedral resonances in the region at 0 ppm. The Utah bituminous coal (APCS #6) was found to have the most tetrahedral aluminum, about one-third the area of the total aluminum signal (see Table 1 and

Fig. 2c). The values in Table 1 were determined from the MAS spectra. Static and VAS spectra were also run to confirm that the octahedral resonances were devoid of spinning sidebands that would influence the relative intensities of the tetrahedral and octahedral aluminum centerbands.

In addition to the spectra of the raw coals, NMR measurements were performed on density separated materials. The predominantly carbonaceous portion of the Argonne Premium Coals was separated from the heavier, mineral-rich material to provide information on the distribution of the different layer silicates closely associated with the organic matter. Minerals that are finely dispersed within the organic matrix were found to float in a solution of density 1.42 g/cm^3 (aqueous solution of CsCl and Brij-35), while the larger, mineral-rich material sank after centrifugation. We chose APCS #6 as one of the first coals to separate because it had the most favorable tetrahedral to octahedral aluminum ratio. The aluminum-27 NMR spectrum (Fig. 2d) of the mineral concentrate obtained from density separated APCS #6 shows at least a two-fold increase in intensity of the tetrahedral resonance over that observed for the raw coal (Fig. 2c). Moreover, this treatment apparently does not alter the structure of the minerals. The aluminum-27 or silicon-29 NMR spectra of raw APCS #3 (Illinois #6) are essentially the same as the corresponding spectra of its mineral concentrate obtained by sink-float, Figs. 1a and 1c, 2a and 2b. The effect of concentrating the mineral matter is apparent from the reduction in time needed to acquire the spectra; the raw coal required approximately 15 hours of total acquisition (Fig. 2c) while the mineral concentrate required less than 2 hours (Fig. 2d). In addition, the silicon-29 spectrum of the carbonaceous upper portion of the same coal (Fig. 1d) (50 hours total accumulation time) shows substantial differences in mineral composition compared with spectra of the raw coal or mineral concentrate.

These spectra of the density separated fractions clearly demonstrate that a different mix of minerals is intimately dispersed in the organic matrix compared to that found for the detrital material. We are currently pursuing additional density separations in order to see whether spectral differences can be observed with mesh size or whether other Argonne Premium Coals show interesting behavior. We feel these initial results demonstrate that NMR can yield valuable information about the type of mineral matter present in coal and that the technique has the potential to resolve mineral matter intimately associated with the organic portion of coals from epigenetic minerals that are present.

ACKNOWLEDGMENT

The authors would like to thank C.-Y. Choi for his advice and the many helpful discussions on density separation.

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TABLE 1. Distribution of Tetrahedral and Octahedral Aluminum Found in the Argonne Premium Coal Samples (APCS) by Solid-State Aluminum-27 NMR.^a

Coal	Number	% Tetrahedral	% Octahedral
Upper Freeport mv bituminous	(APCS #1)	25	75
Wyodak subbituminous	(APCS #2)	8	92
Illinois No. 6 hvC bituminous	(APCS #3)	10	90
Pittsburgh No. 8 hvA bituminous	(APCS #4)	13	87
Pocahontas lv bituminous	(APCS #5)	32	68
Utah bituminous	(APCS #6)	33	67
Stockton hvA bituminous	(APCS #7)	10	90
North Dakota lignite	(APCS #8)	5	95

^aEstimated error is $\pm 5\%$.

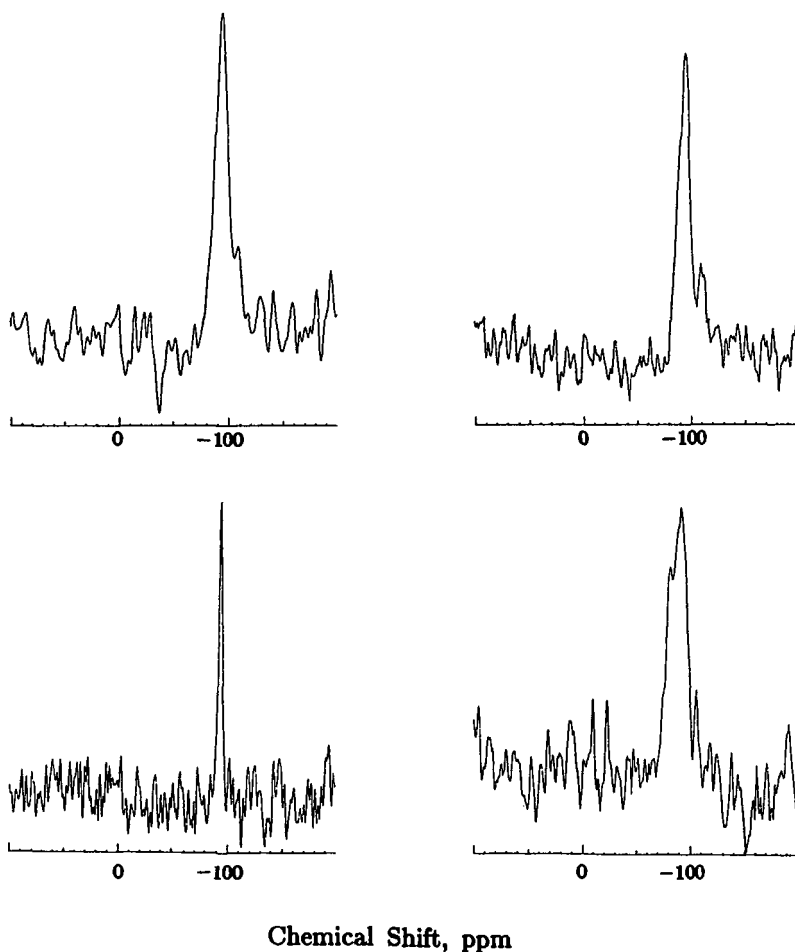


Figure 1. Silicon-29 MAS NMR spectra of raw APCS #3: (a) spin-echo and (b) CP; and spin-echo spectra of its density separated (c) sink (mineral-rich) and (d) float (organic-rich) material.

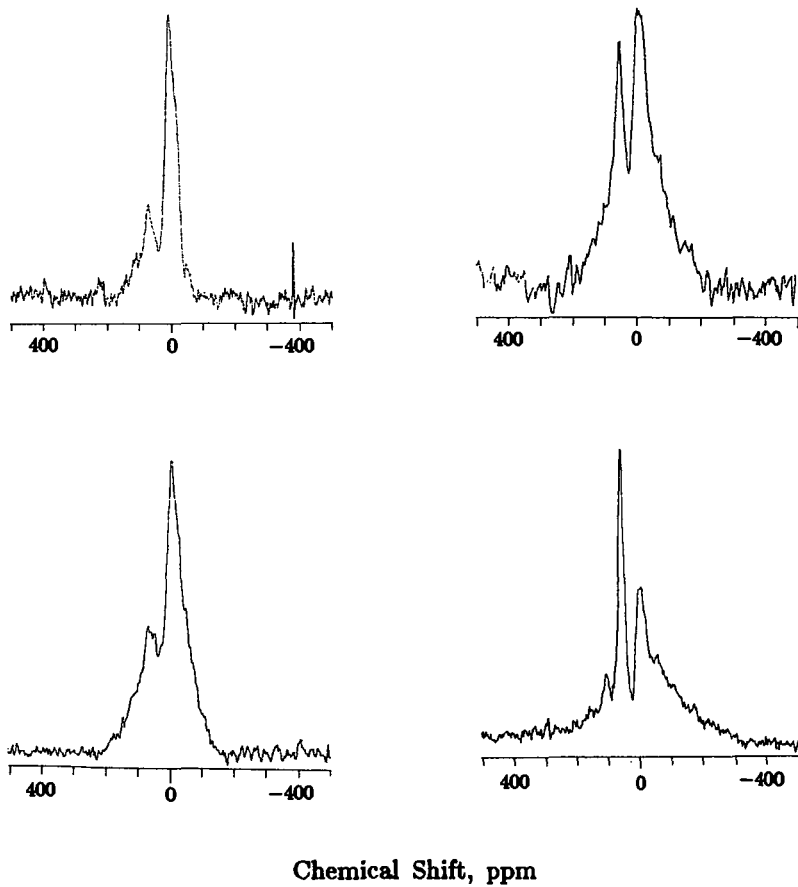


Figure 2. Aluminum-27 MAS NMR spectra of (a) raw APCS #3 (b) sink of APCS #3 (c) raw APCS #6 and (d) sink of APCS #6.

An EPR Study of Nitroxide Spin Probe Doped Illinois no. 6 Coal From
the Premium Coal Sample Program: Reactive Site Distribution

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INTRODUCTION

The conversion of coal by an economically feasible catalytic method is an important area of research for our future energy requirements. However, knowledge of the coal structure is necessary before optimum use can be made of the catalyst. For instance, the catalyst must be able to diffuse into the coal sample so that hydrogenation catalysis can occur from within as well as the normal surface catalysis. This requires an estimation of the size, number, and shape of the pores in the coal before and after swelling with different solvents and the number distribution of different reactive sites within a coal sample. In the past, efforts have been made to estimate the total void volume (porosity) and distribution of pores by measuring the moisture content of coal and penetration by mercury as a function of pressure (1). It was concluded that the internal surface of coal is associated with a capillary system of < 4 nm pores connected by 0.5 - 0.8 nm passages. Liquid and vapor sorption studies (2) of porosity and internal surface of coal suggest that a definable pore structure may not exist and that accessibility is a better term to use.

Recently, we reported (3) a method to determine the relative pore (accessibility) size and number distribution in selected high-volatile bituminous coal samples by diffusing nitroxide spin probes of different shapes, varying in diameter or length from 0.47 nm to 3.5 nm, into the swellable pores of the coal samples. The relative spin probe concentration was measured by Electron Paramagnetic Resonance (EPR) methods for each sized spin probe. From these measurements, a relative number and size distribution was estimated for the swellable pores of Mary Lee (MRI, PSOC-271) and Black Creek (MRI) coal seams of Alabama and the Illinois no. 5 (PSOC-699) seam. The coal samples were obtained from the Mineral Resources Institute (MRI) at the University of Alabama and the Penn State Coal Sample Bank (PSOC) at Penn State University. The pore sizes deduced from these studies were consistent with those deduced by mercury penetration studies carried out as a function of pressure. It was found (3) that the size and number distribution of pores deduced from the spin probe concentration is different for each coal seam. For instance, there are 5 times as many swellable pores of the shape of a long chain stearamide (length 3.4 nm) in Mary Lee coal as there are in Black Creek coal, while there are 18 times as many short chain (1.2 nm length) cylindrical pores and only 0.3 times as many medium length cylindrical pores. Further details of the size and number

distribution reported earlier, can be found in Table 2 of reference 3.

It was also observed (3) that the nitrogen coupling in the principal z direction of the incorporated spin probe (those with a diameter or length greater than 1 nm) exhibited a temperature dependence above 250 K that is largely a result of librational motion of the nitroxide moiety about the N-C bond. Below 250 K, the temperature dependence of the nitrogen coupling is like that found for spin probes in solids that exhibit an equilibrium between a nonbonded and a hydrogen bonded state; the hydrogen bonded state exhibiting the larger coupling. The possibility of hydrogen bonding may suggest a mechanism whereby the spin probes are incorporated in the porous structure of the coal samples.

While the earlier study (3) dealt largely with determining the number distribution for swellable pores with diameters between 0.46 nm and 3.5 nm, no attempt was made to study reactive site distributions and whether a hydrogen bonding mechanism is an important mechanism for spin probe incorporation in pores of the coal samples.

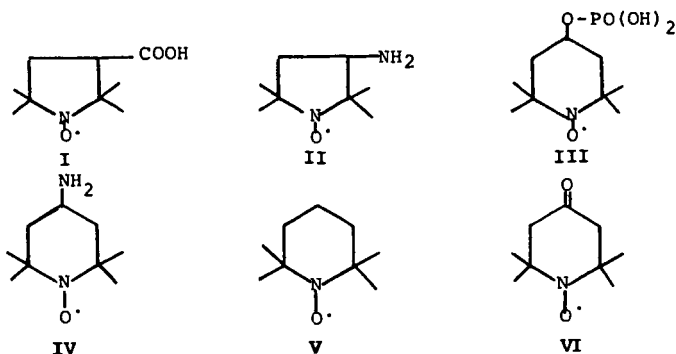
Thus this study reports the results of a series of similar but small sized spin probes (~ 0.6 nm in diameter), each containing a different reactive substituent, to determine the number distribution of reactive sites containing acid, phenol and amine substituents. The smaller size of the spin probes with reactive sites, will permit a measure of all accessible sites with diameters greater than approximately 0.6 nm.

In addition, a study was made to differentiate hydrogen-bonding to the nitroxyl group from that of a substituent group in swellable pores with diameters of approximately 0.4-0.6 nm.

EXPERIMENTAL

Samples of Mary Lee (MRI), Black Creek (MRI) and Illinois no. 5 (PSOC-669) high-volatile bituminous coal from the stock samples previously studied (3) and samples of Illinois no. 6 obtained from the Premium Coal Sample Program at the Argonne National Laboratory were selected for study. The proximate and ultimate analyses for all coals except Illinois no. 6 have been previously given (3) while the ash free percentage by weight values of the Illinois no. 6 sample equal C (79%), H (5.6%), O (9.7%), and S (5.4%). All coal samples were stored under a blanket of N₂ except Illinois no. 6 which arrived in sealed ampoules under humid nitrogen. Upon opening, the samples were stored under N₂ or argon.

A 30 mg sized, dried and unmodified sample of each coal was added to a 10⁻³ M solution of nitroxide spin probe in toluene. Six different spin probes (I-VI), obtained from Molecular Probes, Inc. Junction City, Oregon, were used. These probes were selected because they are all of similar size and because spin probes I and III react with amines, spin probes II and IV react with acids and phenols and spin probes V and VI can be used to distinguish between hydrogen bonding to a ketone and to a nitroxyl group.



Each coal and spin probe mixture was stirred vigorously at 50-60°C in a sealed flask. After 16-18 hours, the excess toluene was suction-filtered off and the remaining solid material evacuated to dryness to collapse the coal around the spin probe. The dried material was washed with ethanol (a nonswelling solvent) to remove any spin probe attached to the exterior of the coal, suction filtered, packed into an EPR sample tube, evacuated and sealed. The prepared spin-probe-doped coal sample was stored under liquid nitrogen.

EPR powder spectra were recorded on a Varian E-12 EPR spectrometer interfaced to an IBM-XT for each sample as a function of temperature (77-335 K) using the standard Varian variable-temperature and liquid nitrogen accessory. The magnetic field was calibrated using a Bruker ER 035 M NMR Gaussmeter and the microwave frequency was measured with a model H/P 5246 L frequency counter. EPR spectra were recorded on disk with an IBM-XT using the EPRDAS software program from Adaptable Laboratory Software. For spectra recorded only on graph paper, input to disk was achieved by use of a Kurta Tablet Digitizer using Sigma-Scan software. A computer program has been developed using the ASYST language (MacMillan Software) to calculate the relative concentration of spin probes in different coal samples in the presence of the severe spectral overlap by the EPR spectrum of the undoped coal. The computer program has also been expanded to analyze temperature dependent coupling constants in terms of hydrogen-bond equilibrium or/and small amplitude librational motion. Output is to a H/P 7440 A Plotter.

RESULTS:

EPR spectra obtained from coal samples containing spin probes gave rise to a spectrum similar to that shown in Figure 1, consisting of an intense central line due to undoped coal (curve B) and, at high gain (curve A), resolved powder EPR lines at high and low magnetic fields due to the z tensor component of the nitrogen hyperfine coupling (A_{zz}) arising from the nitroxide spin probe dopant. The separation between the high and low field component equals $2A_{zz}$. The relative spin concentrations were determined by integrating the low field peak. The relative spin probe concentration is given in table I for probe I (reacts with amines), probe IV (reacts with acids and phenols), probe V (hydrogen bonding only to the nitroxyl group) and

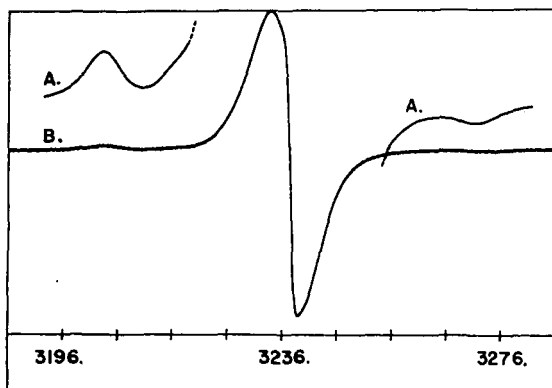


Figure 1. EPR spectrum of a spin probe in a sample of Black Creek coal at (A) high gain (X10) and (B) at low gain (X1) at 300 K.

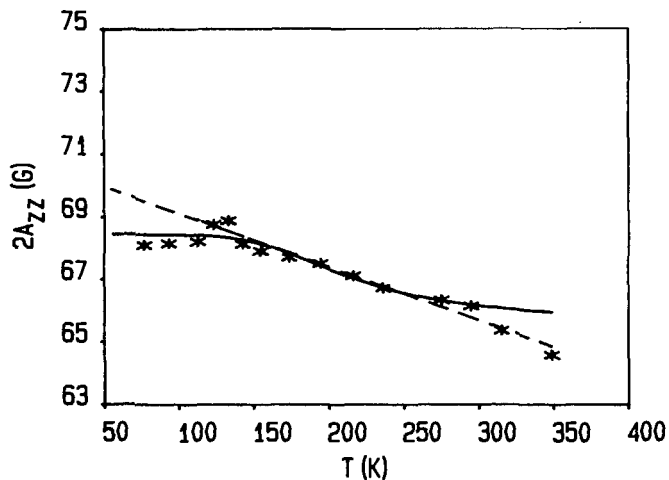


Figure 2. $2A_{zz}$ against temperature for spin probe VIII (DCT-Tempamine) incorporated in a sample of Illinois no. 6 (premium coal): *, experimental data; ----, librational model; —, hydrogen-bond equilibrium.

probe VI (hydrogen-bonding to ketone and nitroxyl groups). The results for spin probes II and III are not reported here.

Table I. Relative Site Distribution for Spin Probes I, IV, V and VI.

Coal Sample	Spin Probes*			
	I (COOH) Base/acid	IV (-NH ₂) reaction	NO V (sub.) hydrogen bonding	VI (=O)
Mary Lee	220	67	24.0	1.0
Black Creek	230	1550	5.3	5.0
Illinois no. 5	100	53	4.1	17.0
Illinois no. 6	14	164	4.9	11.0

*Relative spin probe concentration normalized to probe VI in Mary Lee coal.

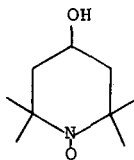
Notably, the ratio of pores containing acid or phenolic groups to those containing amine groups is 1/3; 6.7/1; 0.5/1; and 12/1 for Mary Lee, Black Creek, Illinois #5 and Illinois #6 respectively. In addition, Black Creek coal has approximately 25 more sites containing acid or phenol groups than either Mary Lee or Illinois no. 5 coal samples, and nearly an order of magnitude greater than that found in the Illinois no. 6 sample. The sites containing amine functions are similar except for the Illinois no. 6 sample for which the amine concentration decreases by nearly an order of magnitude. It is interesting to note that more spin probe V (factor of 23) can be incorporated into Mary Lee (only one site available for hydrogen-bonding), than spin probe VI (2 sites for spin probe hydrogen-bonding), while the presence of hydrogen-bonding sites does not seem to matter for spin probe incorporation in Black Creek coal, but is a factor of 4 greater for VI in Illinois no. 5 and a factor of 2 greater for incorporation of VI in Illinois no. 6. It is apparent from these measurements that the presence of an additional site for hydrogen bonding is of little importance in determining the amount of spin probe incorporated in small (0.4 to 0.6 nm) pores in samples of Mary Lee and Black Creek coal.

The separation between the high and low field EPR lines ($2A_{zz}$) for each spin probe exhibits a temperature dependence between 350 and 77 K. It was previously shown for bulky or long chain spin probes (3) that at high temperature, the temperature dependence of A_{zz} is due to librational motion of the NO group of the spin probe with respect to the CNC plane of the nitroxide ring and is given by Equation 1

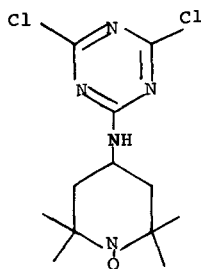
$$2A_{zz}(t) = A_{zz}^0 [1 + \cos(kt/E_a)]^{0.5} \quad 1)$$

where E_a = the barrier to librational motion and A_{zz}^0 is a temperature independent hyperfine coupling. At temperatures below 270 K, the temperature dependence can be fit to an equation derived from the assumption that the spin probe exists in an hydrogen-bond equilibrium between two states, one with a larger coupling due to hydrogen-bonding and the second to a non-bonding state. This type of dependence follows the solid line in Figure 2 and is noted by the near temperature independence at low temperature (3). Similar behavior is observed for spin labels tightly bound within hemoglobin (4).

Temperature dependent studies of 4-aminotempo-(IV) in Illinois no. 6 coal, Mary Lee, Black Creek, and Illinois no. 5, showed a very interesting dependence. A near perfect fit to the librational model (dashed line in Figure 2) occurred for the $A_{zz}(t)$ value observed for IV in the Illinois no. 6, Mary Lee and Black Creek and a small dependence of a hydrogen-bond model was observed for IV in Illinois no. 5 coal. In addition when the smaller spin probe tempo, (VII),



VII



VIII

(the OH substituted for NH_2 in IV) was incorporated in Illinois no. 6 it gave a temperature dependence of A_{zz} that was clearly due only to a librational motion as the temperature dependence follows a straight line relationship. However the temperature dependence of DCT-tempamine, (VIII) incorporated in Illinois no. 6 exhibits a behavior like that found for other large spin probes - librational behavior at high temperature and evidence of hydrogen-bond equilibrium below 200 K (See Figure 2).

In Table II are given the energy barriers to librational motion of the spin probes deduced from the temperature dependent hyperfine coupling parameter A_{zz} . Although the variation is not large, the large sized spin probe VIII does have a higher barrier to rotation than IV, as would be expected for a large size probe trapped in the swellable coal pores.

Table II: Energy Barrier to Librational Motion of Spin Probes in Four Coal Samples.

Coal	Spin Probe	E_a (kJ/Mole)
Illinois no. 6	IV	6.69 (± 0.04)
Illinois no. 6	VII	7.57 (± 0.04)
Illinois no. 6	VIII	8.59 (± 0.04)
Mary Lee	IV	8.61 (± 0.03)
Black Creek	IV	7.88 (± 0.02)
Illinois no. 5	IV	7.26 (± 0.04)

CONCLUSION

The reactive site distribution detected by spin probes approximately 0.6 nm in diameter, varies from coal seam to coal seam. The detected acid and phenolic sites in Black Creek Coal and the Illinois No. 6 coal (Premium Coal Sample Program) exceed the detected amine sites by approximately an order of magnitude while slightly more amine than acid or phenolic sites are detected in samples of Mary Lee and Illinois no. 5. On the other hand, the greatest number of reactive acid and phenolic sites were detected in Black Creek coal. The ability for the coal pore to hydrogen bond to a spin probe was shown not to be an important process for incorporating spin probes in Mary Lee and Black Creek coal and only a slight factor in samples of Illinois no. 6, and Illinois no. 5. Because of this the number of swellable pores containing spin probes V and VI was at least an order of magnitude lower than the reactive sites containing I and IV. Spin probes V and VI exhibited large librational motion in the swellable pores.

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